PB92-216894

Characterizing Heterogeneous Wastes: Methods and Recommendations (March 26-28, 1991)

Nevada Univ., Las Vegas

Prepared for:

Environmental Monitoring Systems Lab., Las Vegas, NV

Feb 92

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Office of Research and
Development
Washington DC 20460

U.S. Department of
Energy
Washington DC 20585

EPA/600/R-92/033
February 1992

EPA

PB92-216894

Characterizing Heterogeneous Wastes:

Methods and Recommendations

Co-Sponsors:

EPA

United States Environmental Protection Agency
Environmental Systems Monitoring Laboratory
Office of Research and Development
P.O. Box 93478
Las Vegas, Nevada 89193-3478

United States Department of Energy
Office of Technology Development
Washington, DC 20585-0002

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U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before comple

1. REPORT NO. EPA/600/R-92/033

2.

3. PB92-216894

4. TITLE AND SUBTITLE
CHARACTERIZING HETEROGENEOUS WASTES: Methods and Recommendations

5. REPORT DATE February 1992

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
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1200 Sixth Ave., Seattle, WA 98101

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
U.S. Environmental Protection Agency
Office of Research and Development
EMSL-LV, P.O. Box 93478, Las Vegas, 89193

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA/600/07

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Sites where the wastes are of large size or varied composition, including landfills and drum dumps, present severe difficulties to investigators attempting to collect representative samples to facilitate site cleanup decisions. This document serves as the workshop proceedings. It summarizes the study planning tools, sampling design strategies now in use, identifying the advantages and disadvantages of each. Areas that would benefit from research or development, or the adoption of new approches, are identified. Regulatory definitions are augmented with practical working definitions. The discussion of the study planning process emphasizes the establishment of reasonable goals and the participation of the decision maker, and the technical specialists. Project planning for heterogeneous waste characterization is an iterative process. There are many statistical models that are potentially useful for characterizing these sites, though only a few have seen wide use. Standard QA/QC methods can be adapted to enhance the quality of heterogeneous waste data. Many field methods are currently employed. These range from excavation and hand-sorting of large objects to sophisticated instrumental methods for characterization or screening. Several promising field technologies are in development. These emphasize non-intrusive characterization, because consideration for worker health and safety dictates minimal contact with the waste. In the laboratory, the three basic strategies for handling heterogeneous samples are to separate them, homogenize them, or analyze the entire sample. Exhaustive documentation is essential. Laboratory waste management and personnel safety are areas of concern when heterogeneous wastes are handled.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	**19. SECURITY CLASS** *(This Report)* UNCLASSIFIED	**21. NO. OF PAGES** 161
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	**22. PRICE**

EPA/600/R-92/033
February 1992

CHARACTERIZING HETEROGENEOUS WASTES:

METHODS AND RECOMMENDATIONS

March 26–28, 1991

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Cooperative Agreement No. CR 814701
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EPA

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NOTICE

The information in this document has been funded in part by the U.S. Environmental Protection Agency under an assistance agreement with the U.S. Department of Energy. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document.

ABSTRACT

The U.S. Environmental Protection Agency and the U.S. Department of Energy conducted a workshop in March 1991 to examine methods for characterizing heterogeneous wastes contaminated with hazardous chemicals and/or radionuclides. Sites where the wastes are of large size or varied composition, including landfills and drum dumps, present severe difficulties to investigators attempting to collect representative samples to facilitate site cleanup decisions. This document serves as the workshop proceedings. It summarizes the study planning tools, sampling design strategies, and field and laboratory methods now in use, identifying the advantages and disadvantages of each. In addition, areas that would benefit from methodological research or development, or the adoption of new approaches, are identified. Pertinent regulatory definitions are assembled and augmented with practical working definitions. The discussion of the study planning process emphasizes the establishment of clear, reasonable goals and the active participation of the decision maker, along with program, field, and laboratory specialists. Project planning for heterogeneous waste characterization is an iterative process, with each step building on knowledge gained in previous steps. There are a large number of statistical models that are potentially very useful for characterizing these sites, though only a small number have seen wide use. Standard environmental QA/QC methods can be adapted in several ways to enhance the quality of heterogeneous waste data. A plethora of field methods is currently employed. These range from excavation and hand-sorting of large objects to sophisticated instrumental methods for remote characterization or contaminant screening. Several promising field technologies are now in development. These emphasize non-intrusive characterization, since consideration for worker health and safety often dictates minimal contact with the heterogeneous waste. In the laboratory, the three basic strategies for handling heterogeneous samples are to separate them, homogenize them, or analyze the entire sample. Exhaustive documentation of sample appearance and condition, and the sample preparation method, are essential. Laboratory waste management and assurance of personnel safety are areas needing special care when heterogeneous wastes are handled.

For each aspect of heterogeneous waste characterization there are new methods that bear research or are already under development. In addition, there are entirely new approaches to site characterization that could substantially accelerate the remediation of sites containing heterogeneous waste.

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ACRONYMS

AA	atomic absorption spectrometer
AEC	Atomic Energy Commission
ANSI	American National Standards Institute
ARAR	Applicable or Relevant and Appropriate Requirement (under CERCLA)
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
CAA	Clean Air Act
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CERCLIS	Comprehensive Environmental Response, Compensation and Liability Information System
CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
CWA	Clean Water Act
DDA	Differential die-away
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
DQO	data quality objective
DT	Deuterium-Tritium
ELES	external laboratory evaluation sample
EM	electromagnetic
EMSL-LV	Environmental Monitoring Systems Laboratory-Las Vegas
EPA	U.S. Environmental Protection Agency
FD	field duplicate
FES	field evaluation sample
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
FEMP	Fernald Environmental Management Project
FOCS	fiber optic chemical sensors
FRB	field reagent blank
FT-IR	Fourier-transform infrared spectroscopy
FTE	full-time equivalent (person-years)
FWPCA	Federal Water Pollution Control Act
GC	gas chromatography
GPR	ground-penetrating radar
H&S	health and safety
HLRW	high level (radioactive) waste
HMTA	Hazardous Materials Transportation Act
HRC	Harry Reid Center for Environmental Studies
ICP	inductively coupled plasma spectrometry
LA-ICP-AES	laser ablation inductively-coupled plasma atomic emission spectrometry
LEAFS	laser excited atomic fluorescence spectrometry
LIBS	laser induced breakdown spectroscopy
LIF	laser induced fluorescence
LLRW	low level (radioactive) waste
LSC	liquid scintillation counting

ACRONYMS *(Continued)*

MQO	method quality objective
MS	mass spectrometry
NAA	neutron activation analysis
NACEPT	National Advisory Council for Environmental Policy and Technology
NAREL	National Air and Radiation Environmental Laboratory
NEPA	National Environmental Policy Act
NIST	National Institute of Standards and Technology
NORW	naturally-occurring radioactive waste
NPDES	National Pollutant Discharge Elimination System
NPL	National Priorities List
NQA	Nuclear Quality Assurance
NRC	Nuclear Regulatory Commission
OAR	Office of Air and Radiation
ORD	Office of Research and Development
ORME	other regulated materials exempted
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration
OSW	Office of Solid Waste
OVA	organic vapor analyzer
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyl
PEG	polyethylene glycol
PID	photoionization detector
PRB	preparation rinsate blank
PRP	Potentially Responsible Party (under CERCLA)
PS	preparation split subsample
PSR	particle size reduction
PVC	polyvinyl chloride
QA	quality assurance
QAMS	EPA's Quality Assurance Management Staff
QAPjP	Quality Assurance Project Plan
QC	quality control
RAS	CLP Routine Analytical Services
RCRA	Resource Conservation and Recovery Act
ROD	Record of Decision
RQ	Reportable Quantity
RS	routine sample
SARA	Superfund Amendment and Reauthorization Act
SDWA	Safe Drinking Water Act
SERS	surface enhanced Raman scattering
SOP	standard operating procedure
TCLP	Toxicity Characteristic Leaching Procedure
TRU	transuranic (nuclear material)
TSCA	Toxic Substances Control Act
USATHAMA	U.S. Army Toxic and Hazardous Materials Agency

ACRONYMS *(Continued)*

VOA	volatile organic analysis
VOC	volatile organic compound
XRF	x-ray fluorescence spectroscopy

ACKNOWLEDGEMENTS

This document is the product of a workshop sponsored by the U.S. Environmental Protection Agency and the U.S. Department of Energy in March 1991. Project manager for the EPA was Ken Brown of the U.S. EPA's Environmental Monitoring Systems Laboratory-Las Vegas. Project manager for the U.S. DOE was John Mathur. The Harry Reid Center for Environmental Studies (HRC; formerly the Environmental Research Center) of the University of Nevada-Las Vegas conducted the project under Cooperative Agreement No. CR 814701. The UNLV project manager was Gretchen Rupp and the workshop coordinator was Kathleen Lauckner.

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Chapter 1

Introduction

Gretchen Rupp

Background

"Heterogeneous wastes" include those materials otherwise known as debris, solid waste, trash, and rubbish. Because of their relatively large particle size and varied composition, heterogeneous wastes are often much more difficult to characterize than more uniform materials such as soils and sludges. Many types of heterogeneous wastes are found on industrial, municipal, and federal waste sites in the United States. These include municipal trash, demolition debris, waste construction materials, containers such as drums, tanks, and paint cans, the solid wastes from laboratories and manufacturing processes, and post-consumer wastes such as transformers, battery casings, and shredded automobiles. These wastes may be inert materials such as rock, glass, or concrete; labile organic matter such as wood and food wastes; or miscellaneous items such as rubber, plastic, or asbestos wastes. Potentially-contaminated structures and utilities pose problems similar to those of heterogeneous wastes, and similar strategies may be employed for characterizing heterogeneous wastes and contaminated structures.

Heterogeneous wastes are found on tens of thousands of sites across the U.S. The U.S. Environmental Protection Agency (EPA) has estimated that approximately 6000 municipal landfills were in operation in 1986 (1); many more dumps or landfills had been filled and closed by then. Heterogeneous wastes contaminated with hazardous chemicals are found on National Priorities List (NPL) sites, sites regulated under the Resource Conservation and Recovery Act (RCRA), and sites listed in the Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS). Information compiled within EPA's ROD database indicates that more than half of all NPL sites contain such wastes; the proportion is probably similar for RCRA sites and CERCLIS sites (those uncontrolled hazardous-waste sites that have been inventoried but have not been placed on the NPL). The U.S. Department of Energy (DOE), which has undertaken a major cleanup program for its facilities, has jurisdiction over thousands of sites contaminated with radionuclides, hazardous chemicals, or both. Many of the sites include contaminated heterogeneous wastes. Over 1.4 million drums containing radioactive or hazardous chemical wastes must be characterized preparatory to remedial action at the DOE sites (2).

Characterizing heterogeneous wastes presents a number of special problems. The principal difficulty arises in attempting to obtain representative samples of a material composed of disparate elements. Customary sample segregation, compositing, and homogenization schemes used to characterize water, soil, or sludge are often completely inappropriate for these materials. Waste particle size frequently poses difficulties. According to standard sampling theory, obtaining a representative sample of varied items in the size range of a centimeter or larger may entail collecting tens or hundreds of pounds of material. Large objects cannot be made to fill standard sample containers, so that bulky items exhumed from within waste piles and placed in standard sample jars quickly lose volatile organic compounds (VOCs) to the headspace. Few analytical laboratories have the capability of performing leaching tests on raw samples of heterogeneous materials because of the large volumes involved and the difficulty of conserving VOCs. Nor are laboratories well equipped to reduce samples of large, varied items to the tiny, homogeneous aliquots used for analysis. In cases where sample grinding and homogenization are possible, they may be inappropriate. The contamination of heterogeneous waste particles is often superficial, so that contaminant concentration data expressed on a mass basis do not properly reflect the human health risk posed by the waste.

Many field methods have been used to characterize heterogeneous wastes, but the available methods are often insufficient for the task. While there are several remote methods for characterizing containerized wastes, they cannot give a complete picture of the hazardous chemicals contained within a drum. Samplers must often resort to opening containers and hand-segregating objects in the field. Worker health and safety considerations often preclude thorough characterization activities. Data quality assessment is hampered by the lack of performance evaluation samples for heterogeneous materials.

When a decision is to be made concerning the disposition of a hazardous waste site, the decision-maker first establishes the required confidence level in the correctness of the decision. The data needs, data quality objectives, and all site characterization planning follow from this. When heterogeneous wastes are to be characterized, many of the above-mentioned problems may be encountered. Project planners frequently discover that a study sufficient to achieve a high level of confidence would incur excessive costs, labor requirements, or risks to field workers. Clearly, methodological research and development, and possibly entirely new approaches to these sites, are needed.

Purpose and Scope of this Document

In recent years hazardous-waste professionals have accumulated a great deal of experience with heterogeneous wastes. The purpose of this report is to synthesize what they have learned and the methodological gaps they have identified. Specifically, it is a response to the need expressed by EPA and DOE personnel for an examination of:

- sampling design strategies and field and laboratory methods currently in use, their range of application, and their shortcomings;
- areas where research, development, or new approaches could improve the selection of available tools; and
- technologies or sampling designs used in other disciplines that might be adapted to the characterization of heterogeneous wastes.

Care has been taken to craft this report in accordance with current and evolving EPA and DOE policy, especially that promulgated by EPA's Office of Solid Waste. However, the document does not represent any form of policy decision on the part of either agency. As they appear herein, the words "must," "shall," "should," and "may" should be construed as the opinions of technical experts, not the dictates of law.

This document originated in an invited workshop, conducted by EPA and DOE in March 1991, where participants deliberated in several topical work groups. The discussions herein reflect the experiences and opinions of more than 100 technical professionals who have planned and conducted heterogeneous waste studies. The field is an evolving one, and the workshop made it clear that professional opinions vary on the applicability of different methods. Insofar as possible, this report attempts to cover the full range of techniques available and experiences with those techniques. Consequently the reader will not generally find the document espousing the use of any one approach or set of methods, and, indeed, there are differences in approach between chapters.

This document is principally targeted towards the needs of project managers. It should be of most use to those responsible for planning and conducting waste characterization studies, as well as agency personnel who regulate such studies and contractor personnel responsible for oversight. Agency decision-makers should also find these materials helpful as they attempt to frame answerable questions concerning the contamination of heterogeneous wastes. Finally, the report's research and development recommendations should be of interest to those responsible for these activities within EPA and DOE.

Official agency guidance concerning the general techniques to be used in waste-site investigations is available elsewhere and is not repeated herein. This document focuses on methods specific to heterogeneous materials and, where appropriate, the adaptation of standard methods to these materials. The techniques that are discussed can be applied to characterizing municipal solid waste and non-hazardous industrial waste. However, there is a strong emphasis on wastes contaminated with hazardous chemicals and/or radionuclides because of the added risks and characterization difficulties they pose (learning what solid wastes are present is only a small step towards ascertaining the nature and degree of contamination).

The discussion in this document assumes that initial site surveys have been carried out and a detailed waste characterization study is to be performed. No size limit has been placed on the waste materials that are considered. Contaminant characterization of structures is not explicitly dealt with because the unique aspects of building decontamination have been discussed elsewhere. Nor are soil characterization methods dealt with, although on a certain scale soil is a heterogeneous medium. A great number of soil characterization methods have been developed in recent years, but this report is concerned with materials that vary on a larger scale than soil.

The scope of discussion herein has been circumscribed by the type of question a waste characterization study may be designed to answer. Among the questions most commonly asked are:

- Is the container of waste (or the waste pile) hazardous *as a unit*?
- Does the container or pile *include regions of material that are hazardous*?
- What is the likely effectiveness of each potential remedial measure?
- Is the treatment process working properly?

- Do residuals from the treatment process meet standards?

This document focuses on characterization efforts designed to answer the second of these questions. Generally stated, the question is: ***Does the unit of waste contain areas of contamination that exceed the specified action level?*** This may be the most difficult of the five questions, and advancing the "state of the science" in answering this question will provide benefits in all aspects of heterogeneous waste characterization. The discussions herein have been further targeted towards two specific waste site scenarios. The first scenario is uncontainerized heterogeneous waste: waste piles, dumps, landfills, or buried deposits. The second scenario is a "worst case" instance of containerized waste (Figure 1-1). This is a drum of heterogeneous waste similar to those encountered by the thousand at DOE facilities. The drum contains metal, plastic, liquid-filled glass containers packed in paint cans, laboratory tissues, and other solid wastes. The contaminants present within the solid wastes may be radioactive or chemical or both, and their identity is not known *a priori*.

Contents

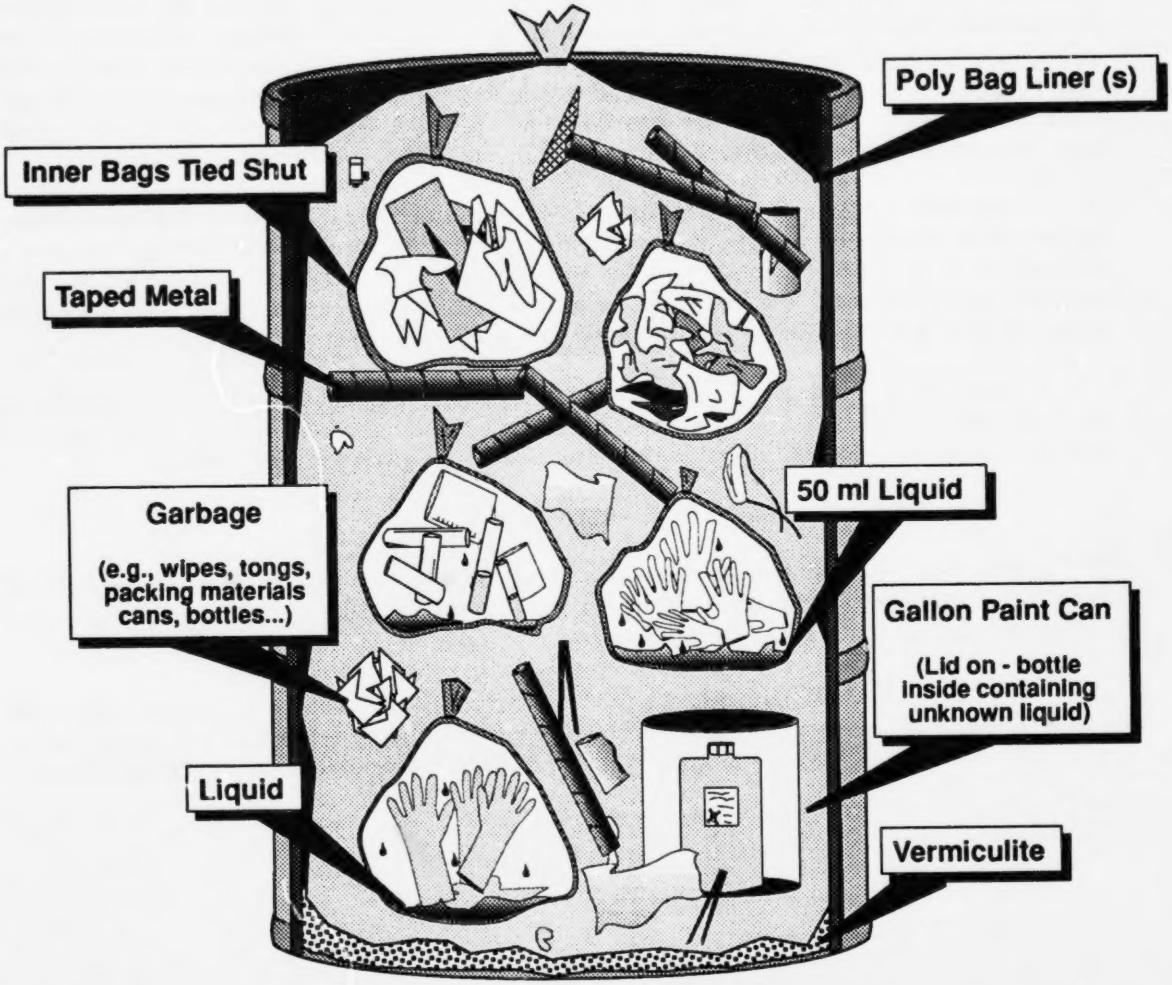
The next chapter presents a set of definitions pertinent to the characterization of heterogeneous wastes. In addition to the regulatory definitions, there are colloquial or common-sense definitions for a number of terms. These cannot supercede the regulatory definitions, but they provide a functional complement to the often-arcane definitions codified in law. This set of definitions provides a common basis for all of the chapters that follow.

Chapter 3 deals with project planning as performed for heterogeneous waste characterization. Establishing data needs and data quality objectives is the first topic handled. The discussion steps through the "DQO process" that EPA has developed for planning site investigations, using drummed hazardous and radioactive wastes as an example. This is followed by an examination of the more detailed, practical considerations that enter into the selection of a strategy for characterizing heterogeneous materials. The issues of formulating a site model, selecting an appropriate statistical sampling design, and protecting worker health and safety are discussed.

Chapter 4 covers data quality assessment issues specific to heterogeneous wastes. Methods for evaluating data bias and precision are discussed. The question "How many samples are enough?" is addressed. Heterogeneous-waste quality assurance issues in need of research or development are presented.

In Chapter 5, the field activities of the waste characterization study are discussed. Both containerized and uncontainerized wastes are covered. The various non-intrusive methods and those that involve handling the waste are described. The strengths and limitations of current methods are set forth, and developing technologies that may offer promise are described.

Chapter 6 deals with the laboratory aspects of the problem. Because analytical methods are the same for heterogeneous wastes and conventional environmental media, this chapter concentrates on the laboratory preparation of heterogeneous waste samples: sample receipt, subsampling, and extraction. Quality control procedures unique to these wastes are evaluated, and the special prob-


Poly Bag Liner (s)
Inner Bags Tied Shut
Taped Metal
50 ml Liquid
Garbage
(e.g., wipes, tongs, packing materials cans, bottles...)
Gallon Paint Can
(Lid on - bottle inside containing unknown liquid)
Liquid
Vermiculite

Additionally may contain:
asbestos gloves, respirator cartridges,
photographic materials

Total "free"
liquid < 1% by volumne

Figure 1-1. The worst-case drum of heterogeneous wastes.

lems they pose for laboratory waste management are discussed. Methods for handling materials with radioactive and VOC contamination are examined.

Each of the foregoing chapters includes recommendations for research that could benefit that particular stage of a heterogeneous waste characterization study. Chapter 7 enlarges on these and considers the characterization of heterogeneous waste in a holistic perspective. Specific ways to aid characterization studies through technology transfer and enhanced communication are discussed. Regulatory impediments are identified, and suggestions for surmounting them are given. New ideas for enhancing the overall characterization and remediation process are set forth.

Appendix A presents a hypothetical case history, a site containing thousands of waste drums that must be characterized. The discussion steps through the process of surveying the drums, defining the decision to be made, establishing the data needs and data quality objectives, and designing the study itself. The example is intended to reasonably portray the difficulties inherent in such studies without invoking overwhelming detail or esoteric mathematics.

Appendix B is a discussion of statistical techniques that may be useful for characterizing heterogeneous wastes. The most promising techniqus are rated with respect to their degree of development and potential utility. Literature references are given for each method.

References

1. U.S. Environmental Protection Agency. 1988. Report to Congress: Solid Waste Disposal in the United States. Volume II. Office of Solid Waste and Emergency Response, Washington, DC. EPA/530-SW-88-011B.

2. Harmon, L.H. 1991. Heterogeneous waste characterization needs and requirements of the Department of Energy. Panel presentation to the Heterogeneous Waste Characterization Workshop, Las Vegas, March 26, 1991. U.S. DOE Office of Technology Development.

Chapter 2

Definitions

Fred Haeberer and Jeff van Ee

Introduction

Characterization of hazardous wastes requires a clear understanding of the overall objectives behind the data collection effort. Legislation and regulations often form a basis for those objectives with the definition of key terms being an important consideration.

Definitions of terms can come from a variety of sources. Legislation and regulations, dictionaries, publications for the layperson and professional publications, and professional societies are some of the more common sources. Occasionally, there may be no consensus on the definition of a term. This lack of consensus might be construed to mean that there is no definition. Sometimes a term may be so commonly used that little thought is given to whether a documented, authoritative definition exists. In meeting the objectives of a data collection effort, it is important that everyone involved in the various aspects of the effort have a common language and that there be clear definitions of terms.

Members of the Definitions work group came from several different organizations. A number of different perspectives and professional experiences were represented within the group. The group's objective was to develop a common language for the Workshop on Characterization of Heterogeneous Waste to facilitate communication among the individual work groups and allow workshop participants to address the difficult issues involved in the characterization of heterogeneous waste. Obviously, one of the first tasks was to define "heterogeneous waste."

Definitions development by the work group began with the examination of pertinent, existing definitions found in laws, regulations, dictionaries, and professional publications. These definitions were examined for their appropriateness to the characterization of heterogeneous waste. If a legally-defined term was judged sufficient by the scientists and engineers involved in the characterization of heterogeneous waste, the definition was accepted. If a legally-defined term was found to be unacceptable to the Definitions work group membership, then either a layman's definition or one from a professional source was put forward to accompany the legal definition. Debate and discussion of these definitions was often lengthy, with most participants realizing that the achievement of consensus for a single definition of a term was neither practical nor wise.

The list of definitions provided below identifies the source of each definition. In some cases, definitions provided in the listed references have been modified slightly to make them more readable and achieve consensus. Users of the list of definitions are advised to consult the original source if the fine points of a definition become important.

While considerable effort was expended in obtaining an accurate, up-to-date, complete list of definitions of terms that might commonly be used in the characterization of heterogeneous wastes, much more effort needs to be expended. Several courses of action are recommended.

Present-day computer hardware and software allow for lists of definitions to be easily assembled, updated, and conveyed to interested persons. "Hypertext" is a relatively new term for information presented on a computer screen, where specific items can be marked for further, more detailed information. Hypertext allows for documents to be written at different levels for different people, aiding in the communication of terms that have different levels of understanding and different sources. Furthermore, a definition often may include terms that require additional definition. Consequently, it is recommended that a hypertext version of the list of definitions be developed and periodically updated.

Many of the terms used in the characterization of heterogeneous waste require further clarification and standardization, especially across agencies. Consequently, it is recommended that a follow-up definitions workshop be held for professionals from a variety of backgrounds to collaborate in further defining these terms and those from related areas.

Finally, the work group felt that, once a list of definitions is developed, it will be important for that list to serve as a source of definitions in the development or revision of laws and regulations.

Whether the following list of definitions meets the needs of users outside of the workshop remains to be seen. Further modification of the list can be expected, with new terms being added and existing terms being expanded and clarified. The weight given to this list will depend on how often people refer to the list and incorporate the definitions into their daily vocabulary. If all of the participants in the workshop, in their respective work groups, adopt the list, then considerable progress toward establishing a uniform language will have been made. At the beginning of the workshop, there were far more definitions of terms than at the end. Time will tell whether those remaining definitions prove to be workable and worthy of incorporation into other lists of definitions in other situations.

Definitions

Past regulatory development practice has resulted in the redefinition of some standard, non-technical English words. Furthermore, different government agencies can define the same non-technical word to mean different things (e.g., see Ground water and Groundwater below). This practice may jeopardize the public's right to know and, more importantly, its right to understand environmental legislation and must be avoided. The involved agencies must be encouraged to negotiate terminology that is consistent with common usage and mutual understanding.

As a partial remedy, careful usage of technical jargon is proposed. For example, "hazardous waste" should retain its natural meaning, which is applicable to all wastes that can be potentially damaging to human health or the environment. The specialized EPA term should be referred to as "Hazardous waste according to 40 CFR xx, Part xx," or "RCRA hazardous waste." The definitions below that are not preceded by a citation were developed by the work group and are intended to be operational rather than legal or enforceable.

The primary source of the terms and definitions presented in this glossary is the Code of Federal Regulations (CFR). Additional sources include the Environmental Protection Agency's "Quality Assurance Glossary and Acronyms" (EPA QA Glossary, reference 3), Department of Energy Orders (e.g., DOE 5820), Webster's 9th Collegiate Dictionary, "Principals of Environmental Sampling" by Lawrence H. Keith, as well as DOE's "Defense Waste Primer" and "Radiation Primer." A document that was not available to the work group at the time of its meeting is the "Glossary of Environmental Management Terms" compiled by the Training and Management Systems Division of Oak Ridge Associated Universities for the U.S. Department of Energy. This document is highly recommended for persons active in environmental analysis and restoration.

Agricultural solid waste: EPA 40 CFR 243.101
The solid waste that is generated by the rearing of animals, and the producing and harvesting of crops or trees.

Biological wastes:
Non-pathological wastes, waste medical supplies, and non-contaminated media that could support pathogen growth.

Bulky waste: EPA 40 CFR 243.101
Large items of solid waste such as household appliances, furniture, large auto parts, trees, branches, stumps, and other oversize wastes whose large size precludes or complicates their handling by normal solid waste collection, processing, or disposal methods.

Candidate method: EPA 40 CFR 53.1
A method of sampling and/or analyzing environmental matrices for environmental pollutants for which an application for reference method determination or equivalent method determination is submitted in accordance with the CFR.

Characterization:
The determination of the physical, chemical, radiological, and biological properties of a pure substance, compound, or mixture to the extent necessary to support informed decision making.

Characterization method:
A protocol for determining physical, radiological, biological, and chemical properties of a material. Proper usage of this term for waste materials couples the subject material with an appropriate governing regulation; for example:

> "ICP-AES is a useful characterization method for metallic cations at levels specified by the Safe Drinking Water Act."

Commercial solid waste: EPA 40 CFR 243.101
All types of solid waste generated by stores, offices, restaurants, warehouses, and other non-manufacturing activities, excluding residential and industrial wastes.

Composite sample:
A sample composed of several distinct subsamples. Composite samples are often prepared to obtain a more representative sample of the unit or when it is not economically feasible to analyze a large number of individual samples.

Construction and demolition waste: EPA 40 CFR 243.101
The waste building materials, packaging, and rubble resulting from construction, remodeling, repair, and demolition operations on pavements, houses, commercial buildings, and other structures.

Confidence coefficient: QA Glossary (3)
The probability statement that accompanies a confidence interval and is equal to unity minus the associated type I error rate (false positive rate). A confidence coefficient of 0.90 implies that 90% of the intervals resulting from repeated sampling of a population will include the unknown (true) population parameter. See also **Confidence interval.**

Confidence interval: QA Glossary (3)
The numerical interval constructed around a point estimate of a population parameter, combined with a probability statement (the confidence coefficient) linking the interval to the population's true parameter value. If the same confidence interval construction technique and assumptions are used to calculate future intervals, they will include the unknown population parameter with the same specified probability. See also **Confidence coefficient.**

Contact-handled transuranic waste: DOE 5820.2A
Packaged transuranic waste whose external surface dose rate does not exceed 200 mrem per hour.

Control sample:
A sample introduced into a sampling and analytical process to monitor the performance of the system.

Curie (Ci): EPA 40 CFR 190.02
That quantity of radioactive material producing 37 billion nuclear transformations per second (equivalent to 37 billion becquerels (Bq)).

Data performance criteria:
The qualitative and quantitative constraints on the design for data collection that result from the application of the DQO process. These constraints, commonly referred to as DQOs, are used as the basis for the statistical survey design of the data collection effort to insure that the right type and quality of data are collected.

Data quality objective (DQO) process:
The up-front interactive process between the data user (i.e., decision maker) and the data generator (i.e., supporting technical team) which defines the error level (uncertainty) acceptable in the decision/application. See also **Data performance criteria.**

Debris:
The solid remains of a broken or destroyed item.

Decision-maker:
That individual who will represent the regulatory agency or other responsible organization in deciding whether site remediation is needed and selecting the appropriate action(s).

Designated facility: EPA 40 CFR 260.10
A hazardous waste treatment, storage, or disposal facility that has received an EPA permit (or a facility with interim status) in accordance with the requirements of 40 CFR 270 and 124, a permit from a state authorized in accordance with 40 CFR 271, or that is regulated under 40 CFR 261-6(c)(2) or Subpart F of Part 266, and that has been designated on the manifest by the generator pursuant to Section 262.20.

Detection limit:
The lowest concentration or amount of a target analyte that can be determined by a single measurement to be different from zero or background level at a defined level of probability. The detection limit is generally recognized to be sample-matrix and measurement-method dependent. See also **Method detection limit**.

Disposal:
The systematic and orderly placement, storage, distribution, or transformation of wastes.

Disposal facility:
A facility at which waste is intentionally placed, stored, distributed, or transformed.

EPA 40 CFR 260.10, 270.2
A facility at which hazardous waste is intentionally placed and at which the waste will remain after its closure.

Disposal site - radiological: EPA 40 CFR 192.01
The region within the smallest perimeter of residual radioactive material (excluding cover material) following completion of control activities.

Disposal site - hazardous, including mixed waste:
A location where hazardous waste is disposed.

Dose equivalent: EPA 40 CFR 190.02
The product of absorbed dose and appropriate factors to account for differences in biological effectiveness due to the quality of radiation and its spatial distribution in the body. Also see DOE Order 5400.5, "Radiation Protection of the Public and the Environment," February 8, 1990.

Equivalent method: QA Glossary (3)
Any method of sampling and/or analysis demonstrated to result in data having a consistent and quantitatively known relationship to the results obtained with a reference method under specified conditions, and formally recognized by the EPA.

Extremely hazardous substance: EPA 40 CFR 355.20
A substance listed in Appendices A and B of 40 CFR 355.

Certain hazardous substances that, when released at levels above their CERCLA Reportable Quantities, require notification of local and state emergency response authorities due to the potential for serious irreversible health effects. See also **Reportable quantity**.

Facility - RCRA: EPA 40 CFR 260.10
All contiguous land, and structures, other appurtenances, and improvements on the land used for treating, storing, or disposing of hazardous waste. A facility may consist of several treatment, storage, or disposal operational units (e.g., one or more landfills, surface impoundments, or combinations of them).

Facility - Waste:
All contiguous land, and structures, other appurtenances, and improvements on the land, used for treating, storing, or disposing of waste. A facility may consist of several treatment, storage, or disposal operational units (e.g., one or more landfills, surface impoundments, or combinations of them).

Field measurement:
A determination that is made on-site.

Field screening:
Rapid, qualitative, or semi-quantitative on-site measurements.

Final closure: EPA 40 CFR 260.10
The closure of all hazardous waste management units at the facility in accordance with all applicable closure requirements so that hazardous waste management activities under 40 CFR Parts 264 and 265 are no longer conducted at the facility unless subject to provisions in Section 262.34.

Food waste: EPA 40 CFR 243.101
The organic residues generated by the handling, storage, sale, preparation, cooking, and serving of foods, commonly called garbage.

Generator: EPA 40 CFR 260.10
Any person, by site, whose act or process produces hazardous waste identified or listed in 40 CFR Part 261 or whose act first causes a hazardous waste to become subject to regulation.

Geologic repository: NRC 10 CFR 60.2
A system (site) located in excavated geologic media and intended for disposal of radioactive waste.

Ground water: EPA 40 CFR 260.10
Water below the land surface in a zone of saturation.

Groundwater: NRC 10 CFR 60.2
All water which occurs below the land surface.

Hazard ranking system: DOE 5480.14
The methodology used by EPA to evaluate the relative potential of inactive hazardous waste facilities to cause health or safety problems or ecological or environmental damage.

Hazardous air pollutant:
A substance anticipated to cause either mortality or serious illness when released to the air. The eight hazardous air pollutants are asbestos, benzene, beryllium, coke oven emissions, inorganic arsenic, mercury, radionuclides, and vinyl chloride.

Hazardous chemical, material, or substance:
Any substance which, within a specific concentration range, poses an unacceptable risk to human health or the environment.

Hazardous chemical: EPA 40 CFR 355.20, 370.2
Any chemical defined as hazardous under section 1910.1200(c) of Title 29 of the CFR with certain exceptions.

OSHA 29 CFR 1910, Subpart Z
Any chemical which is a physical hazard or a health hazard. Physical hazards include combustibles, liquids, compressed gases, explosives, flammables, organic peroxides, oxidizers, pyrophorics, and reactives. A health hazard is any chemical for which there is good evidence that acute or chronic health effects occur in exposed employees.

Hazardous constituent: EPA 40 CFR 268.2
A constituent listed in Appendix VIII of 40 CFR 261.

Hazardous material: DOT 49 CFR 171.8; HMTA, Sect. 1802
A substance or material, including a hazardous substance, which has been determined by the Secretary of Transportation to be capable of posing an unreasonable risk to health, safety, and property when transported in commerce, and which has been so designated.

Any of the more than 16,000 materials appearing in the Hazardous Materials Table in 49 CFR 172.101.

Hazardous substance: DOT 49 CFR 171.8
A material, including its mixtures and solutions, that:

(1) Is listed in Appendix to 49 CFR 172.101;
(2) Is in a quantity, in one package, which equals or exceeds the reportable quantity (RQ) listed in the Appendix to 49 CFR 172.101; and
(3) When a mixture or solution
    (i) For radionuclides, conforms to paragraph 6 of the Appendix to 49 CFR 172.101.
    (ii) For other than radionuclides, is in a concentration by weight which equals or exceeds the concentration corresponding to the reportable quantity of the material, as shown in the table found in 49 CFR 171.8.

Hazardous substance: EPA 40 CFR 300.5
Any substance designated by sections 307(a) or 311(b) of the CWA, section 102 of CERCLA, section 3001 of the Solid Waste Disposal Act, Section 112 of CAA, or Section 7 of TSCA.

DOE EH-231-003/0191 (January 1991)
"Hazardous" Terminology

Any substance that, when released to the environment in an uncontrolled or unpermitted fashion, becomes subject to the reporting and possibly response provisions of the Clean Water Act and CERCLA.

Hazardous waste: DOT 49 CFR 171.8

Any material that is subject to the Hazardous Waste Manifest Requirements of the Environmental Protection Agency specified in 40 CFR Part 262.

EPA 40 CFR 243.101, 260.10, 261.3, 302.3

Any waste (or combination of wastes) which poses a substantial present or potential hazard to human health or living organisms due to its lethal, non-degradable or persistent nature or because it may cause or tend to cause detrimental cumulative effects.

DOE EH-231-003/0191 (January 1991)

A solid waste that must be treated, stored, transported, and disposed of in accordance with applicable requirements under Subtitle C of RCRA.

Hazardous waste constituent: EPA 40 CFR 260.10

A constituent of a waste that results in its listing as a hazardous waste as per 40 CFR 261, Subpart D, or a constituent listed in Table 1 of 40 CFR 261.24.

Hazardous waste management facility: EPA 40 CFR 270.2

All contiguous land, and structures, other appurtenances, and improvements on the land, used for treating, storing, or disposing of hazardous waste. A facility may consist of several treatment, storage, or disposal operational units (e.g., one or more landfills, surface impoundments, or combinations of them).

Heterogeneous: Webster's 9th Collegiate Dictionary

Consisting of dissimilar or diverse ingredients or constituents.

Heterogeneous samples: Keith (1)

Samples that are not consistent in composition or phase throughout. Heterogeneous samples will not provide representative data when aliquots of them are analyzed.

Heterogeneous waste:

A waste for which a sample of a size suitable for analysis is not representative of the property of concern. Thus a series of samples will have to be analyzed to establish a range of results acceptable to the data user.

High-level (radioactive) waste (HLRW): NRC 10 CFR 60.2

(1) Irradiated reactor fuel, (2) liquid wastes resulting from the operation of the first cycle solvent extraction system, or equivalent, and the concentrated wastes from subsequent extraction cycles, or equivalent, in a facility for reprocessing irradiated reactor fuel, and (3) solids into which such liquid wastes have been converted.

Homogeneous: Webster's 9th Collegiate Dictionary
Of uniform structure or composition throughout.

Imminently hazardous chemical substance or mixture: EPA 40 CFR 61.01
A chemical substance or mixture which presents an imminent and unreasonable risk of serious or widespread injury to health or the environment.

Industrial solid waste: EPA 40 CFR 243.101
The solid waste generated by industrial processes and manufacturing.

Infectious waste: EPA 40 CFR 241.101
Laboratory wastes, surgical operating room pathologic specimens, disposable material of a medical nature from patients suspected to have or diagnosed to have a communicable disease.

Inorganic solid debris: EPA 40 CFR 268.2
Non-friable inorganic solids that are incapable of passing through a 9.5 mm standard sieve that require cutting, or crushing and grinding in mechanical sizing equipment prior to stabilization, limited to the following inorganic or metal materials: metal slag; glassified slag; glass; concrete, masonry, and refractory bricks; metal cans, containers, drums, or tanks; metal nuts, bolts, pipes, pumps, valves, appliances, or industrial equipment; and scrap metal.

Institutional solid waste: EPA 40 CFR 243.101
The solid wastes generated by educational, health care, correctional, and other institutional facilities.

Landfill - RCRA (Subtitle C): EPA 40 CFR 260.10
A disposal facility or part of a facility where hazardous waste is placed in or on land and which is not a pile, a land treatment facility, a surface impoundment, an underground injection well, a salt dome formation, a salt bed formation, an underground mine, or a cave.

Land treatment facility - RCRA: EPA 40 CFR 260.10
A facility or part of a facility at which hazardous waste is applied onto or incorporated into the soil surface; such facilities are disposal facilities if the waste will remain after closure.

Leachate - RCRA: EPA 40 CFR 241.101, 260.10
Any liquid that has percolated through or drained from hazardous or solid waste and has extracted, dissolved, or suspended materials from it.

Level of uncertainty:
The probability of a wrong answer.

Low-level (radioactive) waste: DOE 5820.2A
Waste that contains radioactivity and is not classified as high-level waste, transuranic waste, or spent nuclear fuel or by-product material as defined by this Order. Test specimens of fissionable material irradiated for research and development only, and not for the production of power or plutonium, may be classified as low-level waste, provided the concentration of transuranic is less than 100 nCi/g.

Matrix:
A specific subset of media (e.g., surface water, drinking water, kaolinite) in which the analyte of interest may be contained.

Measurement:
A quantitative determination of one or more properties.

Medium:
The solid, liquid, or gas that serves as a carrier of the analytes of interest.

Method detection limit (MDL): 40 CFR 136, Appendix B
The minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, qualitatively or quantitatively measured, and reported to be greater than zero. [MDLs are method and sample matrix dependent. See **Detection Limit**.]

Mixed waste: Defense Waste Primer
Mixtures containing radioactive and hazardous constituents.

DOE 5820.2A
A waste that is both radioactive as defined by the Atomic Energy Act and hazardous as defined by the Resource Conservation and Recovery Act.

Radiation Primer
Waste that satisfies the definition of LLRW in the Low-Level Radioactive Waste Policy Amendments Act of 1985 and contains hazardous waste that either (1) is listed as a hazardous waste in Subpart D of 40 CFR 261 or (2) causes the LLRW to exhibit any of the hazardous waste characteristics of Subpart C of 40 CFR 261.

Mixture: EPA 40 CFR 355.20, 372.3
A heterogeneous association of substances where the various individual substances retain their identities and can usually be separated by mechanical means. Includes solutions or compounds but does not include alloys or amalgams.

Non-intrusive characterization:
A non-destructive determination that causes no significant change in the material being examined and does not involve physical entry. Used interchangeably with "non-invasive."

Open dump: EPA 40 CFR 241.101
A land disposal site at which solid wastes are disposed of in a manner that does not protect the environment, is susceptible to open burning, and is exposed to the elements, vectors, and scavengers.

Operable unit: EPA 40 CFR 300.6
A discrete part of the entire response action that decreases a release, threat of release, or pathway of exposure.

Pile: EPA 40 CFR 260.10
Any non-containerized accumulation of solid, nonflowing hazardous waste that is used for treatment or storage.

Pollutant: EPA 40 CFR 122.2

Dredged spoil, solid waste, incinerator residue, filter backwash, sewage, garbage, sewage sludge, munitions, chemical wastes, biological materials, radioactive materials, heat wrecked or discarded equipment, rock, sand, cellar dirt, and industrial, municipal, and agricultural waste discharged into the environment.

Quality assessment: EPA (2)

The overall system of activities that provides an objective measure of the quality of data produced.

Quality assurance: EPA (2)

A system of activities whose purpose is to provide to the producer or user of a product or service the assurance that it meets defined standards of quality. It consists of two separate, but related activities, quality control and quality assessment.

Quality Control: EPA (2)

The overall system of activities whose purpose is to control the quality of the measurement data so that they meet the needs of the user.

Quantitation limits

The maximum or minimum levels (concentrations) or quantities of a target variable (analyte) that can be quantified with the required certainty by a single application of the (quality-controlled) measurement method.

Radiation: EPA 40 CFR 190.02

Alpha, beta, gamma, or X-rays; neutrons; and high-energy electrons, protons, or other atomic particles; but not sound or radio waves, nor visible, infrared, or ultraviolet light.

Radioactive material: EPA 40 CFR 190.02

Any material which spontaneously emits radiation.

Radioactive waste:

The byproducts of obsolete or discarded products of nuclear activities that emit radiation.

NRC 10 CFR 60.2

High level waste and radioactive materials other than high level waste that are received for emplacement in a geologic repository.

DOE 5400.3, 5820.2A

Solid, liquid, or gaseous material that contains radionuclides regulated under the Atomic Energy Act of 1954, as amended, and of negligible economic value considering costs of recovery.

DOE 5480.2

Solid or fluid materials of no value containing radioactivity; discarded items such as clothing, containers, equipment, rubble, residues, or soils contaminated with radioactivity; or soils, rubble, equipment, or other items containing induced radioactivity such that the levels exceed safe limits for unconditional release.

Reference method: QA Glossary (3)
A sampling and/or measurement method which has been officially specified by an organization as meeting its data quality requirements.

Reportable quantity:
The maximum amount of material that can be stored, transported, or otherwise handled above which specific regulatory practices are required.

EPA 40 CFR 302 (CERCLA)
The quantity designated for each of 699 hazardous substances under the provisions of section 102 of CERCLA. These spill quantities are for any 24-hour period and include spills on land and in the air in addition to spills in the water.

Repository: DOE 5820.2A
A facility for the permanent deep geological disposal of high level or transuranic waste.

Representative sample: EPA 40 CFR 260.10
A sample of a universe or whole (e.g., waste pile, lagoon, ground water) which can be expected to exhibit the average properties of the universe or whole.

Risk: QA Glossary (3)
The probability or likelihood of an adverse effect.

Rubbish: EPA 40 CFR 243.101
Solid waste, excluding food wastes and ashes, taken from residences, commercial establishments, and institutions.

Runoff: EPA 40 CFR 241.101, 260.10
The portion of precipitation that drains from an area as surface flow.

Sanitary landfill: EPA 40 CFR 241.101
A land disposal site employing an engineered method of disposing of solid wastes on land in a manner that minimizes environmental hazards by spreading the solid wastes to the smallest practical volume, and applying and compacting cover material at the end of each operating day.

Saturated zone: NRC 10 CFR 60.2
That part of the earth's crust beneath the regional water table in which all voids, large and small, are ideally filled with water under pressure greater than atmospheric.

Sediment:
A solid material deposited by water, wind, or glaciers.

Site: EPA 40 CFR 270.2
The land or water area where any facility or activity is [or was] physically located or conducted, including adjacent land used in connection with the facility or activity.

Sludge:
Any mixture of solids, semi-solids, or dense liquid wastes which settle out of solution.

EPA 40 CFR 122.2, 241.101, 243.101, 260.10

Any solid, semi-solid, or liquid waste generated from a municipal, commercial, or industrial wastewater treatment plant, water supply treatment plant, or air pollution control facility exclusive of the treated effluent from a wastewater treatment plant.

Soil:
Naturally occurring geo-organic materials smaller than 2 mm in size, generally found in the surface layer of the Earth and supporting plant life.

Solid waste: EPA 40 CFR 241.101, 243.101, 260.10, 261.2
Garbage, refuse, and other discarded solid materials, including solid waste materials resulting from industrial, commercial, and agricultural operations, and from community activities, but does not include solid or dissolved materials in domestic sewage or other significant pollutants in water resources, such as silt, dissolved or suspended solids in industrial wastewater effluent, dissolved materials in irrigation return flows, or other common water pollutants. It generally does not include mining, agricultural, and industrial solid wastes; hazardous wastes; sludges; construction and demolition wastes; and infectious wastes.

Spent nuclear fuel: EPA 40 CFR 191.02
Fuel that has been withdrawn from a nuclear reactor following irradiation, the constituent elements of which have not been separated by reprocessing.

Standard conditions:
The defined reference point(s) by which ambient measurements are related.

Tank:
A large receptacle for holding, transporting, or storing fluids.

EPA 40 CFR 260.10

A stationary device, designed to contain an accumulation of hazardous waste which is constructed primarily of non-earthen materials (e.g., wood, concrete, steel, plastic) which provide structural support.

Traceable: EPA 40 CFR 50.1
The comparison and certification of a local standard directly or by no more than one intermediate standard, to a primary standard such as a NIST Standard Reference Material or a USEPA/NIST-approved reference material.

Transuranic radioactive waste: EPA 40 CFR 191.02
Waste containing more than 100 nanocuries of alpha-emitting transuranic isotopes, with half-lives greater than 20 years, per gram of waste, with certain exceptions (e.g., high-level wastes).

Unsaturated zone: NRC 10 CFR 602
The zone between the land surface and the regional water table. Generally, fluid pressure in this zone is less than atmospheric pressure, and some of the voids may contain air or other gases at atmospheric pressure. Beneath flooded areas or in perched water bodies the fluid pressure locally may be greater than atmospheric.

Vadoze zone:
Of, relating to, or being water or solutions in the Earth's crust above the permanent groundwater level.

Waste:
Material regarded as damaged, defective, or superfluous by a segment of society.

Also see the following alphabetical listings:

Agricultural solid waste:	EPA	40 CFR 243.101
Bulky waste:	EPA	40 CFR 243.101
Commercial solid waste:	EPA	40 CFR 243.101
Construction/demolition waste:	EPA	40 CFR 243.101
Food waste:	EPA	40 CFR 243.101
Hazardous waste:	EPA	40 CFR 243.101, 260.10, 261.3, 302.3
	DOT	49 CFR 171.8
Infectious waste:	EPA	40 CFR 241.101
Industrial solid waste:	EPA	40 CFR 243.101
Institutional solid waste:	EPA	40 CFR 243.101
Mining waste:	EPA	40 CFR 243.101
Mixed waste:	DOE	Order 5820.2A
Municipal solid waste:	EPA	40 CFR 241.101
Solid waste:	EPA	40 CFR 241.101, 243.101, 260.10, 261.2
Street wastes:	EPA	40 CFR 243.101
Transuranic radioactive waste:	EPA	40 CFR 191.02
Waste waters:	EPA	40 CFR 268.3

Waste form: NRC 10 CFR 60.2
Radioactive waste materials and any encapsulating or stabilizing matrix.

Waste package: NRC 10 CFR 60.2
The waste form and any containers, shielding, packing, and other absorbent materials immediately surrounding an individual waste container.

Waste treatment unit: EPA 40 CFR 260.10
A device which receives and treats or stores aqueous hazardous waste.

Waste unit:
The smallest waste increment which is characterized.

Waste waters: EPA 40 CFR 268.3
Wastes that contain less than 1% by weight total organic carbon (TOC) and less than 1% by weight total suspended solids (TSS), with the exceptions listed in 40 CFR 268.2.

White goods:
Large household appliances: refrigerators, freezers, washing machines, etc.

References

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Chapter 3

Planning the Study

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Introduction

This chapter provides an overview of the heterogeneous waste characterization study, with particular emphasis on planning the study. While the general activities are the same as those for any environmental study, the peculiarities of heterogeneous materials dictate that some planning activities take on critical importance. This chapter presents a generic planning procedure for the characterization of sites having either unconfined or drummed heterogeneous wastes. Because many existing disposal sites contain waste materials stored in drums, the development of a consensus as to a useful procedure for these sites is of substantial and immediate importance. Consequently, most of the examples in this chapter are directed toward defining reasonable and rational protocols for characterizing drums containing waste materials, where there is often significant uncertainty (or even no knowledge at all) as to the actual contents of the drums.

Figure 3-1 presents a generalized scheme of the environmental study process. This flowchart and the text of the chapter represent a concatenation of the work of two groups within the Heterogeneous Waste Workshop, one of which dealt with data needs and data quality objectives, the other of which discussed selecting the study strategy. This figure forms the frame of reference for the chapter. It recognizes that waste characterization is almost always carried out in conjunction with characterization of the surrounding environmental media. Any specific study scheme must be devised in conformity with applicable agency and company guidance and procedures. The investigation of an NPL site, for example, would include numerous Feasibility Study, Risk Assessment, and Community Involvement elements not shown on Figure 3-1. For general information on characterizing hazardous waste sites, investigators should consult EPA and DOE guidance documents and directives (1, 2, 3, 4, 5, 6, 7).

Figure 3-1 depicts a site study as occurring in five phases. There is a preliminary planning stage, in which project scoping occurs and an initial conceptual model of the site and the contamination is formulated. This is followed by a sequence of steps called the "DQO (data quality objectives) process." The DQO process is a study planning process under development by the EPA that formalizes the elements of good experimental design. This process breaks the problem down into discrete, specific questions to be addressed by the study, so that the results can be interpreted with minimal ambiguity and the decision-maker knows the uncertainty associated with the decision.

The DQO process is followed by sampling and analysis design. This involves the consideration of alternative statistical designs for the study, and selection of an optimum design and field and laboratory methods. In reality, study planning almost always requires cycling back and forth more than once between the latter steps of the DQO process and the methods selection steps. The

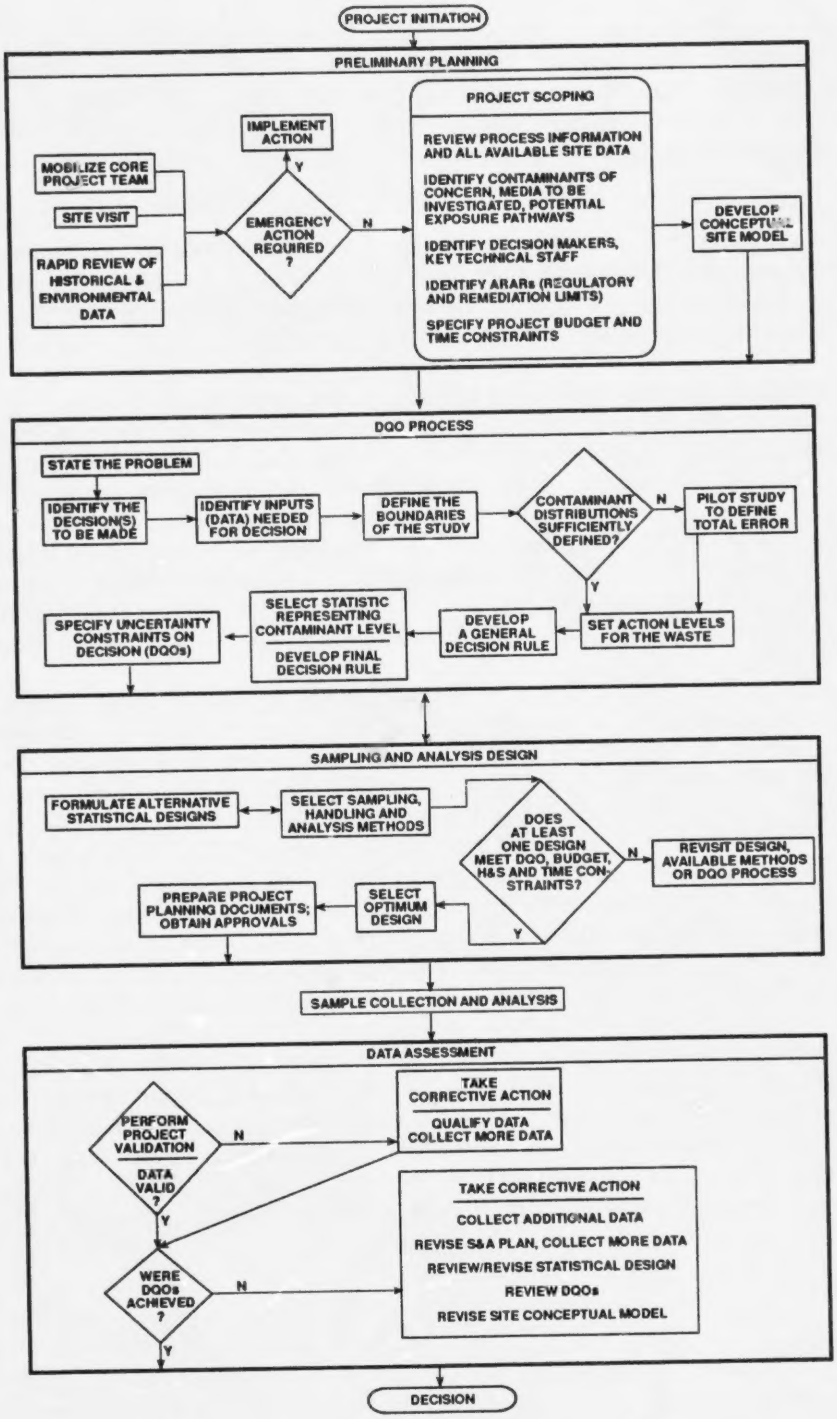

PROJECT INITIATION
PRELIMINARY PLANNING
MOBILIZE CORE PROJECT TEAM
SITE VISIT
RAPID REVIEW OF HISTORICAL & ENVIRONMENTAL DATA
IMPLEMENT ACTION
Y
EMERGENCY ACTION REQUIRED ?
N
PROJECT SCOPING
REVIEW PROCESS INFORMATION AND ALL AVAILABLE SITE DATA
IDENTIFY CONTAMINANTS OF CONCERN, MEDIA TO BE INVESTIGATED, POTENTIAL EXPOSURE PATHWAYS
IDENTIFY DECISION MAKERS, KEY TECHNICAL STAFF
IDENTIFY ARARs (REGULATORY AND REMEDIATION LIMITS)
SPECIFY PROJECT BUDGET AND TIME CONSTRAINTS
DEVELOP CONCEPTUAL SITE MODEL
DQO PROCESS
STATE THE PROBLEM
IDENTIFY THE DECISION(S) TO BE MADE
IDENTIFY INPUTS (DATA) NEEDED FOR DECISION
DEFINE THE BOUNDARIES OF THE STUDY
CONTAMINANT DISTRIBUTIONS SUFFICIENTLY DEFINED?
N
Y
PILOT STUDY TO DEFINE TOTAL ERROR
SET ACTION LEVELS FOR THE WASTE
DEVELOP A GENERAL DECISION RULE
SELECT STATISTIC REPRESENTING CONTAMINANT LEVEL
DEVELOP FINAL DECISION RULE
SPECIFY UNCERTAINTY CONSTRAINTS ON DECISION (DQOs)
SAMPLING AND ANALYSIS DESIGN
FORMULATE ALTERNATIVE STATISTICAL DESIGNS
SELECT SAMPLING, HANDLING AND ANALYSIS METHODS
DOES AT LEAST ONE DESIGN MEET DQO, BUDGET, H&S AND TIME CONSTRAINTS?
N
REVISIT DESIGN, AVAILABLE METHODS OR DQO PROCESS
Y
SELECT OPTIMUM DESIGN
PREPARE PROJECT PLANNING DOCUMENTS; OBTAIN APPROVALS
SAMPLE COLLECTION AND ANALYSIS
DATA ASSESSMENT
PERFORM PROJECT VALIDATION
DATA VALID ?
N
TAKE CORRECTIVE ACTION
QUALIFY DATA
COLLECT MORE DATA
Y
WERE DQOs ACHIEVED ?
N
TAKE CORRECTIVE ACTION
COLLECT ADDITIONAL DATA
REVISE S&A PLAN, COLLECT MORE DATA
REVIEW/REVISE STATISTICAL DESIGN
REVIEW DQOs
REVISE SITE CONCEPTUAL MODEL
Y
DECISION

Figure 3-1. Generalized scheme of the study process.

selection of a statistical design entails a trade-off between what is best from the point of view of statistical theory and what is within the project's cost and risk constraints. These can be driving factors in characterizing heterogeneous materials. It appears that there are many statistical techniques that are potentially applicable to sampling heterogeneous wastes, but most of these have not been tested in this or similar applications. These methods are listed and discussed in Appendix B.

The sampling and sample analysis steps follow. Methods for field characterization or collection of heterogeneous materials are dealt with in Chapter 5. Laboratory analysis is handled in Chapter 6. Most laboratory problems unique to heterogeneous materials are encountered in the sample preparation steps rather than during chemical analysis.

The final study phase shown in Figure 3-1 is data assessment. Chapter 4 suggests specific methods for evaluating accuracy, precision, and completeness of heterogeneous waste data. As in any environmental study, the assessment (both the data validation and all other project validation activities) may lead the project manager to conclude that corrective action is needed. With heterogeneous materials, both inherent and sampling/analysis variability may be much higher than anticipated. Unless this has been discovered and compensated for during the study, it may result in a failure to achieve the DQOs. On reaching the data assessment phase, the project team will have to backtrack and re-evaluate the procedures used, the applicability of the statistical design, the data quality objectives or even the conceptual waste model on which the entire project was based.

This chapter emphasizes periodic re-evaluation throughout the study, to allow for mid-study changes and avoid the need to re-design and re-do the entire study should the DQOs not be attained at the end. It is critical to define early all the questions that are to be answered and all the associated data and informational needs as well as applicable regulations. Furthermore, this is (and should be) an iterative process throughout project planning and implementation. As additional project components are completed and new information becomes available, new questions may arise. If appropriate, these questions should either be incorporated into the plan or become additional projects or project phases. For instance, a drum of liquid solvent waste may be analyzed for a single solvent and water. When the percentage of solvent plus water accounts for only 40% of the drum volume, a new question, "What makes up the remainder of the waste?" emerges. Appropriate actions can then be defined to ensure full characterization of the drum.

At each stage where the judgment is made that more information is needed to answer the question, the project manager will estimate the funding and other resources needed to collect that information. One possible action that is not explicitly shown on the flowchart is always available: the decision to terminate the characterization study, designate all of the waste as exceeding the action levels, and treat or dispose of it accordingly. This decision may be based on cost considerations, concern for worker safety, time constraints, or some combination of these factors.

Preliminary Planning

Initial Activities

The project begins when someone is required to make a decision concerning the disposition of a waste deposit. The decision maker may represent a regulatory agency or the organization responsible for site management. Typical reasons for initiating the waste characterization include: determining whether a regulation is met, whether the material can be stored or shipped, or whether clean-up activities are warranted. The preliminary planning and establishing data quality objectives and sampling design are critical steps prior to beginning the data collection process. Without these steps, considerable effort can be wasted collecting data that do not answer the question or allow a decision to be made.

When characterizing heterogeneous wastes, the early project activities are the same as those for any other site study. The core project team reviews available information about the site and the waste. The decision-maker considers whether an emergency containment/removal action is warranted. In the case of uncontainerized wastes, the primary concern is likely to be whether chemical contaminants can be leached from the wastes by rainwater. For drummed wastes, obvious leakage of fluids is a major concern, as are signs of impending container failure that could allow leakage.

An early site visit by as many members of the project team as possible is of critical importance. Only by seeing the debris pile or the drum dump can the investigators begin to comprehend the heterogeneity that will have to be dealt with in the study. On the site, the project team should search for patterns in the waste placement, begin to think about how to classify the waste into types (populations), and consider what waste handling can and cannot reasonably be done on site. Health and safety hazards posed by unstable debris deposits and leaking containers should be identified. As much information as possible should be gleaned from drum labels.

Project Scoping

Assembling the full project team is an early scoping activity. The ultimate success of the characterization program is directly traceable to the effort that has gone into the project plan. The planning is best accomplished by a team representing several different, well-chosen disciplines. While the team makeup may vary from project to project, it is incumbent on the project manager to choose individuals whose skills and experience cover all of the technical, health and safety, and information aspects that will arise throughout the project, from planning through data reduction to reporting.

The basic technical team for a waste characterization study usually includes a chemist, sampler, statistician, QA/QC specialist, health and safety officer, transportation specialist, and risk assessment evaluator. Other disciplines that may be required (particularly if environmental media are also to be characterized) are meteorology, toxicology, ecology, hydrogeology, various engineering specialties, and computer and data specialties. A civil engineer or construction/demolition specialist may be needed if large debris, structures, piping, or tanks are to be disturbed or moved during the study.

Throughout project planning, it is essential that both management and regulators be included in the process and that they concur with the questions identified and the plan of action required to answer those questions. Management must commit resources, while the regulators will review and approve management's determinations and plans; they may also be issuing permits based on the plan.

The pertinent regulations must be identified early in the planning process. They will drive the final cleanup levels, and hence have important ramifications for data accuracy and precision and required analytical detection limits. In addition, they may prescribe the waste sampling and analysis methods to be used and circumscribe the available remedial methods. In the current regulatory climate, waste is usually assumed to be RCRA hazardous, either by being listed or characteristically hazardous, until it is proven to be otherwise; therefore, RCRA usually applies. The same is true for radioactivity, if there is any evidence that the waste could have radioactive components by association from generative processes or if the source of the waste is simply unknown. When the waste has the potential to be either mixed or radioactive, the number of applicable regulations is multiplied significantly. Normally, the regulations that should be considered are the environmental regulations; however, others may also apply. Those applicable or relevant and appropriate requirements (ARARs) which may apply to the characterization of heterogeneous materials are:

- Resource Conservation and Recovery Act (RCRA), which defines both solid and hazardous waste.
- Toxic Substances Control Act (TSCA), which, for example, regulates a number of hazardous chemicals, including polychlorinated biphenyls (PCBs).
- Clean Water Act (CWA), which is the source of many water quality limits and contains regulations for wastewater treatment and release to receiving bodies of water.
- Federal Water Pollution Control Act (FWPCA), which governs the treatment of industrial wastes and sets standards.
- Safe Drinking Water Act (SDWA), which is the source of groundwater standards and standards for the protection of drinking water sources.
- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as "Superfund," which covers emergency responses and the public right-to-know, as well as clean-up at inactive hazardous waste sites.
- Department of Transportation (DOT) regulations that are concerned with the movement of samples, sampling materials, and waste via public roads, railroads, and air spaces. While there are certain exclusions for routine laboratory samples in these regulations, radioactivity is covered for all materials, and the regulations are very specific concerning data and packaging requirements.
- Atomic Energy Act, interpreted through Department of Energy Orders and Nuclear Regulatory Commission requirements.
- Occupational Safety and Health Act (OSHA) regulations which must be met to ensure worker safety.

Other regulations which sometimes apply arise from:

- Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).
- National Environmental Policy Act (NEPA).
- State Superfund laws.
- Various Corps of Engineer permits and requirements.

- Federal and state facility agreements, memoranda of understanding, complaints, and orders.

As a measure of potential hazard, standards for waste surface contamination levels (as measured by wipe tests) would be very useful for debris. Risk-based action levels of this type have been developed for individual sites, but there are no national regulations embodying such standards.

The project budget and a rough schedule need to be established during project scoping. Heterogeneous waste characterization generally requires more samples to achieve a given level of certainty than does characterization of other materials. Furthermore, the effort required for sample handling and preparation can be considerable, especially if wastes must be hand-sorted in the field. Thus per-sample costs can be high, and the budget may be a serious constraint on the scope of the project. The extra time required to process heterogeneous materials must also be taken into account.

Depending on the site, there may be only a few or very many contaminants of concern. Sites located in industrial districts have often been occupied by multiple businesses producing a wide range of wastes. Privately operated dumps that were permitted to accept only municipal wastes often co-disposed chemical wastes from commercial waste haulers along with garbage and demolition debris. Defining the contaminants of concern at a debris dump entails a combination of screening-level sampling and investigation of site records.

Issues of worker health and safety need to be identified during scoping. The public's right to participate in decisions, the regulator's need for data, and the worker's (sampler's and chemist's) health must always be considered when developing waste characterization strategies. Indeed, health and safety, both radiological and non-radiological, must be a primary concern throughout the characterization process. While the *in situ* characterization may be conducted to determine risk to the public and the environment, worker exposure during field survey, sampling, analysis, and waste disposal usually engenders a larger, though shorter-term, risk.

Historical and process information is gathered at this point and used in developing the preliminary conceptual model of the waste to be sampled. Under federal regulations, knowledge may be substituted for actual sampling and chemical analysis of the waste for the purposes of waste characterization. If a great deal of information is potentially available, it is appropriate for the project manager to do at least a minimal cost/benefit analysis concerning the good to be gained versus the time and resources required to assemble historical information and data instead of sampling and analyzing the waste. In general, the more heterogeneous the waste, the more worthwhile it is to seek out historical and process information. A subjective measure of certainty can be attached to these data, and a comparison with DQOs can be carried out to see whether the initial characterization objectives have been met. However, if a high degree of certainty is required, at least several confirmatory samples characterized by actual chemical analyses will usually be required. It should be noted that, without measurements, only process knowledge allows determination that a waste is a listed hazardous waste under RCRA.

Land titles and survey data are basic to establishing the boundaries of the waste deposit. Sources of land use records, soil types, and aerial photo surveys include:

- County, state, or municipal tax estate and registry offices
- State highway departments and the Federal Highway Administration

- County Extension Agents
- U.S. Soil Conservation Service
- U.S. Geological Survey
- Tennessee Valley Authority
- U.S. Army Corps of Engineers
- U.S. Bureau of Mines

Aerial photographs are particularly useful when they can be compared over time for land disturbances, fencing, and vehicular traffic. Inferences may then be drawn concerning disposal areas, types of wastes and containers, or sources of waste from truck markings and direction of travel.

For wastes generated by specific, known facilities, plant records and interviews are another, more specific source of information. These include:

- purchase records, inventories, and shipping and receiving records
- laboratory analyses and production reports
- industrial hygiene and health physics files
- permits
- interviews with plant managers, engineers, process operators, truck drivers, and maintenance supervisors

An algorithm can be postulated which states that the percent assurance of historical waste data is inversely proportional to its age. All of the major laws governing waste disposal were promulgated in or after 1975; hence, information generated after 1980 has a much higher validity than earlier information. It was around 1980 before the need for waste records with any degree of detail was recognized.

Historical and site data are used to develop a conceptual model of the site and waste (2). Critical questions to be answered in formulating the model are:

- What is the source of the waste?
- How was it emplaced?
- What matrices are affected?
- What is the potential for contamination and with what?
- What was the source and purity of raw materials?
- Who is/was the generator?
- What was the process?
- Why is it a waste?

The model, linking contaminant sources to receptors via pathways, should be as detailed as current information justifies. It should include the contaminated waste as well as the surrounding environmental media. Insofar as possible it should define the actual flux of contaminants from the waste: are they actively leaching into the ground, or is there only potential for leaching? If necessary, the model should distinguish between contaminants emanating from solid wastes and those originating in adjacent or underlying tanks or pits. Dump operators frequently disposed of liquid wastes by allowing them to seep out of unlined pits, and later filled the pits with debris.

There would be little point in devoting the principal study resources to characterizing the debris at such a site; most effort should be focused on the soil and groundwater.

As they develop the site conceptual model, the study planners need to begin considering potential waste management strategies. These will strongly influence the nature and scope of the characterization study. For example, an NPL site that is a municipal landfill with co-disposed hazardous wastes may pose a low-level long-term threat, or waste treatment may be impracticable, according to the expectations of the National Contingency Plan (40 CFR 300.430(a)(iii)). In this case, engineering controls will be the preferred remedial option, and waste characterization will be limited to determining gross landfill properties such as age, physical dimensions, and differential settlement rates. However, if "hot spots" of concentrated contamination are identified within the landfill, treatment of these areas may be required (6). This will call for more thorough waste characterization.

Establishing Data Needs and Data Quality Objectives

Overview of the DQO Process

When environmental data are collected for making regulatory decisions concerning hazardous waste sites, the decision makers must understand the level of assurance associated with these data. To determine the level of assurance necessary to support the decision, an iterative process should be used by decision makers and project planners. This section describes the process of establishing data quality objectives and illustrates the uses of DQOs in the collection of waste site data. The DQO process is by no means the only possible approach to planning a waste characterization study; however, the rigorous, quantitative nature of this process renders it a particularly powerful tool when applied against the variability inherent in heterogeneous wastes. In addition, the process compels active participation by and communication among decision makers, managers, field and laboratory personnel. This team effort is absolutely essential when dealing with these complex materials.

Data Quality Objectives (DQOs, also called Data Performance Criteria) are the full set of constraints needed to design a study, including a specification of the level of uncertainty that a data user is willing to accept in the decision. DQOs are developed using a process that encourages the sequential consideration of relevant issues. Figure 3-2 shows the principal stages in the DQO process. Each of the stages results in an important criterion (or 'product') for the study that describes:

- the problem to be resolved at the site
- the decision needed to resolve the problem
- the inputs to the decision
- the boundaries of the study
- the decision rule
- the uncertainty constraints

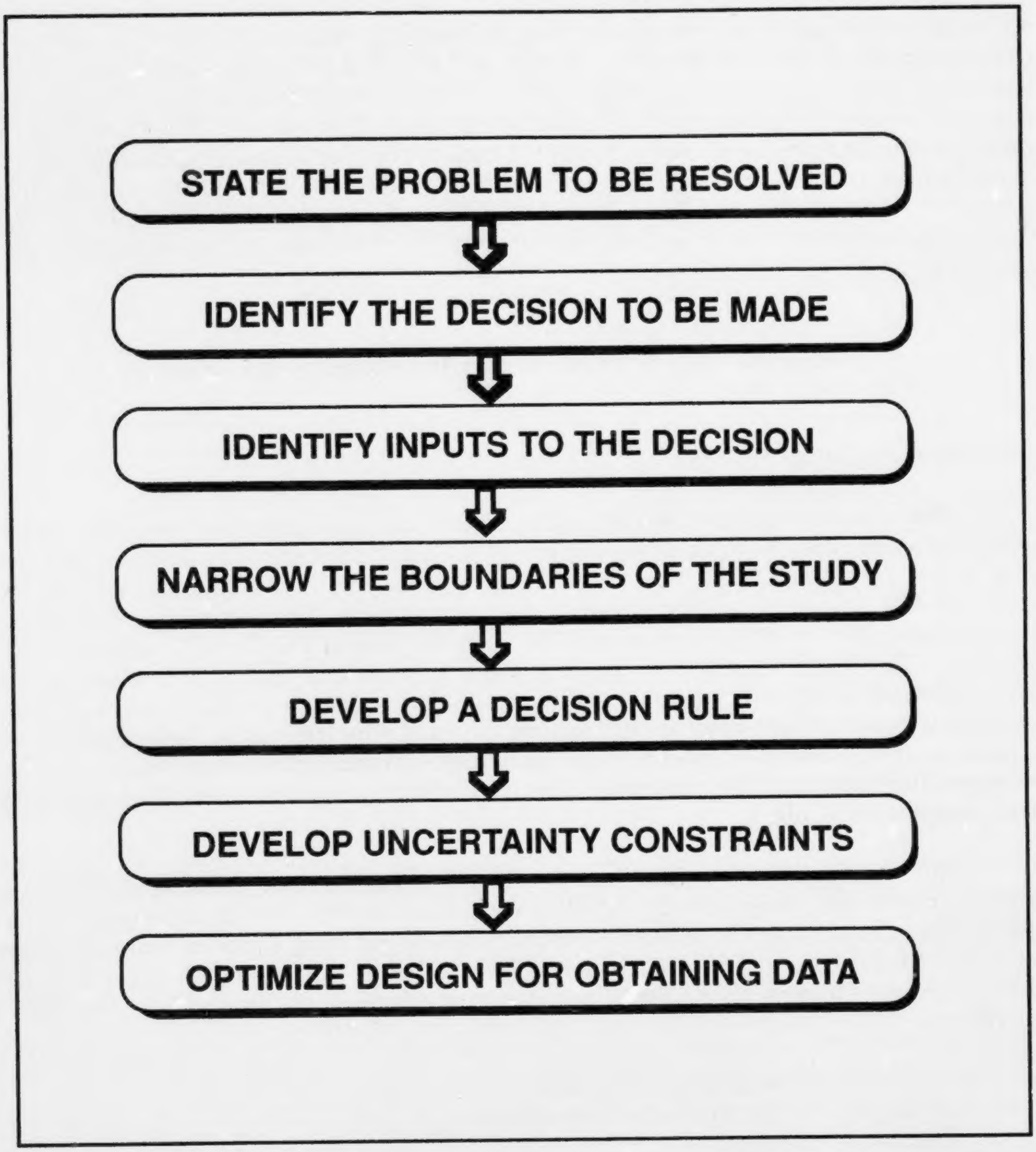

STATE THE PROBLEM TO BE RESOLVED
IDENTIFY THE DECISION TO BE MADE
IDENTIFY INPUTS TO THE DECISION
NARROW THE BOUNDARIES OF THE STUDY
DEVELOP A DECISION RULE
DEVELOP UNCERTAINTY CONSTRAINTS
OPTIMIZE DESIGN FOR OBTAINING DATA

Figure 3-2. Steps in the data quality objectives process.

These constraints or products are the DQOs that will be used to formulate a study design that achieves the desired control on uncertainty, allowing the decision to be made with acceptable confidence. There are several benefits to establishing DQOs:

- The data generated are of known quality.
- DQOs help data users plan for uncertainty. All projects have some inherent degree of uncertainty. By establishing DQOs, data users evaluate the consequences of uncertainty and specify constraints on the amount of uncertainty they can tolerate in the expected study results. The likelihood of an incorrect decision is estimated *a priori*.
- The DQO process facilitates communication among data users, data collectors, managers, and other technical staff before time and dollars are spent collecting data.
- The DQO process provides a logical structure for study planning that is iterative and that encourages the data users to narrow many vague objectives to one or a few critical questions.
- The structure of the process provides a convenient way to document activities and decisions that can prove useful in litigation or administrative procedures.
- The process establishes quantitative criteria for knowing when to stop sampling.

In establishing DQOs, it is important to follow the sequence of stages because the product of one stage is often an input to later stages. However, this process should be regarded as both flexible and iterative; as the study team sees the implications of different products, it should go back as necessary and revise products of earlier stages to incorporate the new concerns.

EPA's "DQO Training Software" provides an interactive opportunity to practice the DQO process. The software is available from the Quality Assurance Management Staff within EPA's Office of Research and Development.

Heterogeneous Waste Example

The following is an example of the DQO process applied to a heterogeneous waste problem. This example was developed at the Heterogeneous Waste Characterization Workshop. To facilitate the reader's understanding of the DQO process, this example has been integrated here into EPA's draft DQO process guidance (8). What follows is an expanded description, based on the guidance, of each of the seven stages in the DQO process with the relevant output from the workshop example provided for each step.

Note that seven principal activities are described below and summarized in Figure 3-2 as the components of the DQO process, while Figure 3-1 shows other activities as part of the process. Some of these additional activities are concurrent or ancillary steps, such as the establishment of site-specific action levels for the contaminated waste. Other activities, like evaluating alternative sampling designs, logically follow establishing the decision rule. In reality, a rough outline of the sampling design is often developed in conjunction with establishing the quantitative uncertainty statements. Establishing the uncertainty rules and statistical design is an iterative process, rather than a sequence of discrete tasks. While the draft EPA guidance treats the evaluation of statistical study designs as part of the DQO process, this chapter sets that activity forth separately so that it can be discussed in greater detail.

The substantial information requirements prevent this example from addressing all the relevant activities at each step of the process, since the example represents a first attempt at developing DQOs for this problem. If more time had been available, the workshop participants would have been able to complete these other activities, refine and reconsider their output for each step of the process, and include other relevant information such as site-specific conditions, disposal costs, disposal capacity, and potential adverse health effects associated with waste mismanagement. Defining DQOs for a real site would involve input and interaction from management and outside interested parties such as the State, local government, and neighbors of the site.

Example

A total of more than 1.4 million drums containing radioactive and hazardous chemical wastes are present at major DOE sites across the U.S. The wastes are not well characterized and are heterogeneous in terms of characteristics and distribution. At many sites, drums are stored in buildings, stacked on the ground and/or covered with dirt. At some sites, the drums have been placed in approximate chronological order of waste generation and, therefore, anecdotal site history and records may provide insights as to their contents.

Characterization of the drums is of primary importance since this information is needed to determine processing/treatment requirements (remedial action). In some cases, drums exhibit the generator's label. DOE assumes all drum labels are accurate and will use them to the extent possible to begin classifying drums into categories (this assumption is not necessarily appropriate for sites not regulated by DOE). In many cases drums are unlabeled and historical information is insufficient to determine their contents. For these drums, new data will be needed to determine how to categorize the drums. The type and variety of wastes we expect to find in drums depends on when the wastes were generated at the sites, waste parentage, and when the wastes were put in the drums. Opening each and every drum for characterization is impractical and may well result in unacceptable worker exposure. Therefore, non-intrusive investigative techniques are preferred. The integrity of the drums is not always clear and is of concern, since some drums have been at sites for many years and some of the contents may be reactive.

The failure of past operations has diminished the public's confidence in management's ability to safely control these wastes. Given the potential magnitude of remediation costs, the resources available for addressing the drum problem must be used efficiently. Interim measures such as redrumming may be considered to prevent a worsening situation due to drum deterioration.

Stage 1: State the Problem To Be Resolved

Product: A description of the problem; initial thoughts on ways to resolve it; and any resource, time, or other practical constraints on the data collection.

Background: The purpose of this step is to describe what is known or expected about the problem, to document the general approach that will be used to address the problem, and to specify practical constraints on the approach to solving the problem.

Activities: State the problem as you currently understand it and sketch out initial ideas on possible ways to resolve this problem. State any ideas or expectations about the problem that are apparent at this point in the process.

Summarize relevant information, including preliminary studies, and indicate the source and reliability of the information.

Develop a list of alternative courses of action (including a no-action alternative, if appropriate) that may be needed to address the problem. Identify existing policies of the regulatory agencies that may influence the alternative actions considered (e.g., agency emphasis on treatment rather than source containment).

Make an initial determination of whether new environmental data will be needed to decide among these alternatives. Determine the importance of social and political considerations to the problem.

If they have not already been identified, name the members of the study team including senior program staff, technical experts, and any senior managers or other representatives of the decision maker whose planning input will be needed during the process to ensure implementation of the study findings. A statistician should either be included in this team or be available to help with portions of this process.

As specifically as possible, describe the constraints on the study that were identified during project scoping. Specify all resource or time limitations for the study, including the anticipated budget and the available manhours. Identify any obvious practical constraints (such as the time of year when data collection is not possible). Identify health and safety considerations that may influence the sampling design or sampling methods.

Example

The planning team, which was made up of representatives from several DOE sites, recognized that the following question has to be addressed prior to determining the appropriate remedial action: "How can the drums at each of these sites be categorized in order to facilitate determining how they should be handled?"

Using the DQO framework, the planning team defined the following drum categories or drum populations based on drum source, contents, and the remedial action appropriate for that category.

1. *Non-radioactive, non-hazardous*
2. *Transuranic (TRU)*
3. *Low-Level Radioactive Waste (LLRW)*
4. *Naturally-Occurring Radioactive Waste (NORW)*
5. *High-Level Radioactive Waste (HLRW)*
6. *Hazardous non-radioactive*
7. *Hazardous TRU*

8. *Hazardous LLRW, and*
9. *Hazardous NORW*

Types 7, 8, and 9 are mixed wastes, by definition. Figure 3-3 illustrates the relationships among these nine categories. Based on the above classification, the DQO team discussed the following project design and drum classification strategy. Radioactive drums will be separated from non-radioactive drums based either on labels or on a non-intrusive investigative technique. All radioactive drums that contain HLRW wastes will be identified based on parentage, separated from all other radioactive drums, and classified as HLRW. The remaining radioactive, non-HLRW drums will be measured to determine if they contain TRU wastes. The first measurement will determine indirectly if the radionuclide specific activity exceeds a specified level. A second test will be conducted on those drums that exceed the specific activity level to determine if the drum contains alpha emitting radionuclides. If the drum satisfies the specific activity and particle emission criteria, the half-life will be measured to determine if it is greater than 20 years. If the drum does not meet the specific activity, particle emission and half-life criteria, it will be placed in a pile (either LLRW or NORW; an additional test may be needed if these two waste types will be disposed of differently) separate from the non-radioactive and HLRW piles. Another study will be designed to determine if any drum designated as containing radionuclide wastes also contains hazardous substances.

The process of identifying drum source and contents determines the category it belongs in and implies the remedial action that is appropriate. Since the consequences of mischaracterizing drums depend on the contents, separate DQOs will be needed for each class of drums. The rest of this example will only address TRU drums. A similar approach would be used to address other classes of waste drums.

Since this is a general example of a DQO, site-specific conditions are not addressed here. In addition, the consequences of mischaracterizing drums are not specifically addressed because issues such as the costs of disposal, disposal capacity, and health effects are site-specific.

Stage 2: Identify the Decision/Question

Product: A statement of the decision that will be made, or the question that will be answered, using waste data. If possible, the decision should be expressed as a determination of whether to take one or more alternative courses of action.

Background: The study will usually produce data that are intended for use in making a decision (e.g., if the waste poses an unacceptable risk, then take remedial action). In a few cases, specific actions and action criteria cannot be identified, possibly because too little is understood about the problem or because this type of problem has not been identified as a priority by the regulatory agency. If specific actions cannot be identified, then these studies fall in the category of research. If they are able to conduct a site-specific research project, the study team should consult EPA's DQO guidance for environmental research (8) to establish DQOs for the study at this point.

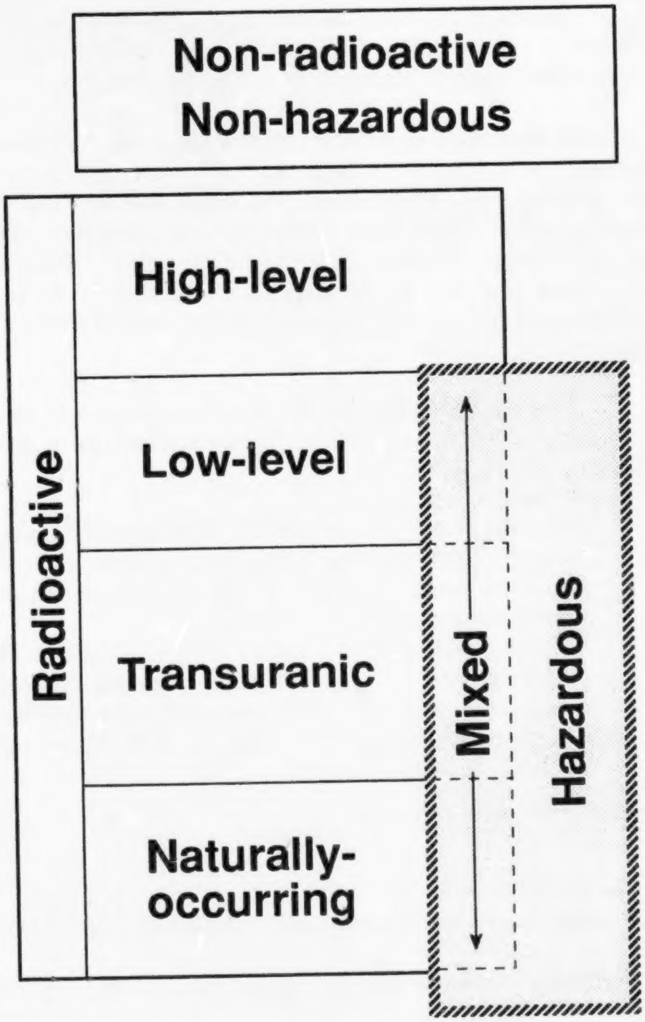

Non-radioactive
Non-hazardous
Radioactive
High-level
Low-level
Transuranic
Naturally-occurring
Mixed
Hazardous

Figure 3-3. Classes of drummed wastes found at DOE sites.

The decision maker (data user) should be involved at this stage and is encouraged to provide general criteria for taking action.

The decision should be stated as narrowly and specifically as possible. If the problem is very complex, then the activities in this step will help the study team identify and organize elements of the larger problem.

Activities: If several separate decisions must be made to address the problem, then begin by mapping out a decision or logic tree. This exercise should reveal the relationship among decision(s). Try to determine the relative importance of each decision to the overall problem. Determine which decisions depend on other decisions. This allows for prioritizing of the decisions. Determine which decisions require new environmental data and the importance of those data to the decision. Use the DQO process for each of the decisions that require new data, starting with the most important decision.

Take the following steps to state the decision or question so that the role of data in taking an action is clear. Broad statements of goals or objectives are not adequate.

- State the range of actions that might be based on the outcome of the study.
- Specify the criteria for taking these actions, including specific "if..., then..." scenarios when possible. If the criteria are not known at this time, then specify how they will be established.
- Frame the decision as a hypothesis to be tested. The hypothesis statement should be qualitative at this point (e.g., null hypothesis: acceptable level of contamination; alternative hypothesis: unacceptable level of contamination); a quantitative statistical formulation of the hypothesis will be developed later in the planning process.

Example

Determine how to classify drums in a manner that facilitates disposition decision making. For this specific example, the following is the statement of the decision with hypotheses for the decision:

Determine whether to classify a drum at a given site as containing TRU wastes.

H_0: *Drum does not contain TRU wastes*
H_1: *Drum contains TRU wastes*

Alternative actions include:

- *dispose of drum containing TRU wastes according to special procedures, or*
- *classify drum as not containing TRU wastes, then determine what other form of radionuclide waste it contains, or*
- *if drum categorization is too hazardous, costly, or time-intensive, treat all drums that are not HLRW as containing TRU wastes and omit the characterization study.*

Stage 3: State the Inputs

Product: The list of variables or characteristics to be measured and other information needed in order to make the decision.

Background: At this stage the study team should identify all variables or characteristics that may be relevant to the decision, and then focus on those that must be measured in order to have the information needed to make the decision.

The initial statement of project objectives may include only those of a short-term nature. However, it is more cost- and time-effective to address both immediate or short-term information needs and future or long-term requirements concurrently. The short-term need may be only to determine whether a waste is a source of radiation; however, upon reflection, long-term information needs, such as level of radiation, source, whether the waste is also RCRA hazardous, etc., are also identified. These concerns expand to storage and shipping regulations.

Activities: Develop a list of variables/characteristics that may affect the decision and separate out those variables that need to be measured in order to make the decision (which action to take) or answer the question.

Select those measurements that together will provide sufficient information to make the decision.

Identify information from other studies, regulations, etc., that is needed to establish the criteria for taking action.

Confirm that each variable can be measured. If not, then determine if it is reasonable to make assumptions about the variable in order to draw conclusions without data. If the necessary assumptions cannot be made, then select an alternative approach that involves different variables. If no practical approach can be developed, then consider shifting the effort to develop the research tools needed to address the problem.

Example

After consideration of factors affecting the decision, the following informational inputs were identified as necessary for making the decision on whether a given drum contains TRU wastes:

(1) Is the drum intact?
(2) Does the drum exhibit a radioactive label?
(3) Does the drum contain radioactive materials?
(4) Is the drum from a HLRW source?
(5) Were TRU materials used at this site?
(6) What is the specific activity of the material in the drum?
(7) Is the radionuclide an alpha emitter?
(8) What is the half-life of the material in the drum?

Measurements will be needed for inputs 6, 7, 8, and possibly 3. Documentation as to parentage will be used for inputs 3 and 4. Visual observations will be used to address inputs 1 and 2.

Stage 4: Narrow the Boundaries of the Study

Product: A description of the population(s) of interest, including a description of the units that make up the population(s) of interest and the spatial and temporal boundaries.

Background: Spatial and temporal boundaries are defined to incorporate all the units that make up the population(s) of interest. In addition, criteria are established for identifying these units and distinguishing them from other similar units (e.g., to locate drums containing radioactive waste, the criteria will specify how to distinguish them from other drums).

The population(s) of interest can be defined as the population(s) of items for which the decision will be made or the question answered. On a heterogeneous waste site, a unit of this population may be a container and its contents, an individual waste item, a volume of uncontainerized waste, or any of the items of a particular type or having certain contamination characteristics.

Activities: Specify the population(s) of interest:

- the units of this population, including the criteria for identifying these units
- the temporal boundaries
- the spatial boundaries

Specify the smallest sub-population for which a separate summary statistic will be calculated. If a separate decision will be made for this group of units, then consider it as a population of interest.

Consider whether the population that is accessible for measurement adequately represents the population(s) of interest. State any assumptions that may be necessary to do so.

At this point, an important step that is often neglected is the pilot study. For conventional environmental media such as soil and water, statistical methods for representing contamination are well established. The variability associated with sampling these media can often be estimated *a priori*. This is not usually the case with heterogeneous wastes. The purpose of the pilot survey is to estimate the inherent variability of contamination of the wastes and the measurement variability introduced by sampling and analysis. This information is critical in developing the uncertainty levels that the decision maker is willing to accept. If these values are not known, an unachievable level of uncertainty may be chosen in the DQO process.

Example

Measurements will be made on all intact drums at a site that has been determined to be radioactive, non-HLRW, but without sufficient historical information to determine if TRU wastes are present. For the half-life measurements, the definition of the boundaries of the survey should include the temporal component of the measurement: the time that will elapse between measurements to determine the half-life of the drums of interest. An individual drum is a unit of the TRU waste drum population.

Measurement of radioactivity will be done by Segmented Gamma Scanner and Passive Active Neutron instruments. A pilot study may be required to collect analytical measurement performance information in order to estimate measurement error. If the results of the pilot indicate that the precision and accuracy of the proposed analytical methods are inadequate or the methods are impractical, then another method will be needed.

Stage 5: Develop a Decision Rule

Product: A quantitative statement that defines how the data will be summarized and used to make the decision or to answer the question, including quantitative criteria for determining what action to take.

Background: The purpose of this stage is twofold:

- to integrate the decision and relevant variables (inputs) into a single statement specifying how environmental data will be summarized and used to make the decision or answer the question within the study boundaries; and
- to indicate what actions will be taken and the criteria for taking those actions.

It is important that someone with statistical expertise be involved at this stage to be certain that the problem is framed in a statistically valid and efficient manner.

The decision rule will be based on tentative or established action levels for the contaminated waste: either ARARs or site-specific risk-based criteria. This decision rule will be reviewed and may require revision after the uncertainty constraints for the decision have been established.

Activities: Describe the summary statistic(s) and how they will be calculated (e.g., mean, range, maximum). Develop a decision rule as an "if..., then..." statement that incorporates the summary statistic, the action criteria (based on the hypothesis test), and the corresponding action(s) that will be taken under various possible scenarios (e.g., if TCLP extracts of piled manufacturing wastes exceed any of the regulatory criteria, the wastes will be treated in place or shipped to a hazardous-waste landfill).

Confirm that all the inputs are incorporated explicitly or implicitly in the decision rule. If not, then reassess the need for them in relation to the decision and either define a more narrowly-focused set of input variables or revise the decision rule to include the full set of variables, as appropriate.

Reconfirm the need for new or additional environmental data to make the decision.

Example

If measurements show that an unlabeled drum exhibits a specific activity > 100 nanocuries per gram, and is an alpha emitter and has a half-life > 20 years, then the drum will be classified as a TRU drum and disposed of accordingly.

H_0: *Drum does not contain TRU waste; specific activity* $\leq$ *100 nanocuries per gram or half-life* $\leq$ *20 years or not an alpha emitter.*
H_1: *Drum contains TRU wastes.*

(Note: all drums labeled as containing TRU waste will be disposed of as TRU waste).

Stage 6: Develop Uncertainty Constraints

Product: The decision maker's expressed desire to control decision errors, stated as limits on the acceptable probability of making an incorrect decision based on the study findings. These may be expressed as acceptable false positive and false negative error rates.

Background: Environmental data collection always involves some error. Therefore, some degree of uncertainty will exist in any decision based on environmental data. In this step, uncertainty constraints are established and stated as acceptable probabilities of making incorrect decisions, i.e., acceptable decision error rates. The uncertainty constraints are used to establish quantitative limits on total study error and corresponding measurement and sampling error constraints. These are used to finalize the decision rule.

Uncertainty constraints should be based on careful consideration of the consequences of incorrect conclusions. The decision maker will need to consider the political, social, and economic consequences of decision errors when setting uncertainty constraints.

The decision maker needs to be actively involved in the development of uncertainty constraints. In addition, the study team should work with a statistician, as necessary, during this step to ensure that the constraints are feasible and complete.

There are two types of decision errors for all studies that use a hypothesis test:

- False positive errors: deciding to take an action when the environmental data incorrectly indicate that a problem exists. In this case, the null hypothesis is rejected when it should be accepted.
- False negative errors: deciding not to take an action when environmental data incorrectly indicate that a problem does not exist. In this case, the null hypothesis is accepted when it should be rejected.

Uncertainty constraints for these types of decisions can be expressed as limits on the acceptable rates of false positive and false negative errors.

Activities: A number of activities are involved in setting acceptable probabilities for decision errors:

- Define false positive [f(+)] and false negative [f(-)] errors for the decision and describe the consequences of each type of error. Note that the consequences can change depending on the size of the error, which may not be well defined.
- Evaluate these consequences according to the relative level of concern or discomfort that they would cause. Environmental, public health, economic, social, and political consequences should all be considered. Differing relative importance may be placed on these consequences depending on the concern of the decision maker, the degree of public interest in the study, etc.
- Determine if false positive or false negative errors are of greater concern.
- Establish, with statistical advice, an acceptable probability for the occurrence of each of these errors. Also, specify a "region of indifference," the area in which one chooses not to control the probability of an incorrect outcome because, under the stated conditions, either false positive or false negative errors are acceptable. This region may be narrow or broad and must be acceptable to the data users.
- Combine the probability statements into a formal statement of the levels of uncertainty that can be tolerated in the results. This formal statement may take the form of a table or a graph.
- Review the decision rule; if necessary, revise or add quantitative measures that will allow the decision uncertainty to be evaluated.

Example

A false positive decision error is deciding that a drum contains TRU wastes when it does not. Consequences of False Positives:

- *Limited disposal capacity designated for TRU wastes will be unwisely and unnecessarily used up*
- *Loss of credibility if the error is discovered by subsequent analysis*
- *Unnecessary costs*

A false negative decision error is deciding the drum does not contain TRU wastes when it does. Consequences of False Negatives:

- *Potential worker, nearby population, and environmental exposure if a drum of waste ruptures*
- *Facility management may be liable and may have to pay penalties*
- *Loss of credibility due to failure to prevent exposure and potential adverse health and environmental effects*
- *Accidents may occur at facility locations where containment is lost*
- *Improper disposal may result in long term exposure.*

Figure 3-4 is the "discomfort curve" that was drawn for the first measurement (the specific activity of the drum contents). The study planners established that either decision is acceptable if the true specific activity is between 80 and 100 nanocuries/gram (i.e., the region of indifference). If the true specific activity is between 60 and 80 nanocuries/gram, it is acceptable to incorrectly judge the drum to exceed the criterion 20% of the time. A 5% false positive rate is acceptable for drums exhibiting a lower specific activity. The planners were more concerned about false negative errors. They specified that for drums exhibiting a specific activity of 100-120 nanocuries/gram, the false negative error rate must not exceed 10%; above 120 nanocuries/gram, it must not exceed 5%.

If the measurement indicates that the drum has a specific activity > 100 nanocuries/gram, then continue with tests for alpha emitter and half-life. Separate discomfort curves would be drawn for each of these measurements. These curves would not necessarily be identical to that for specific activity.

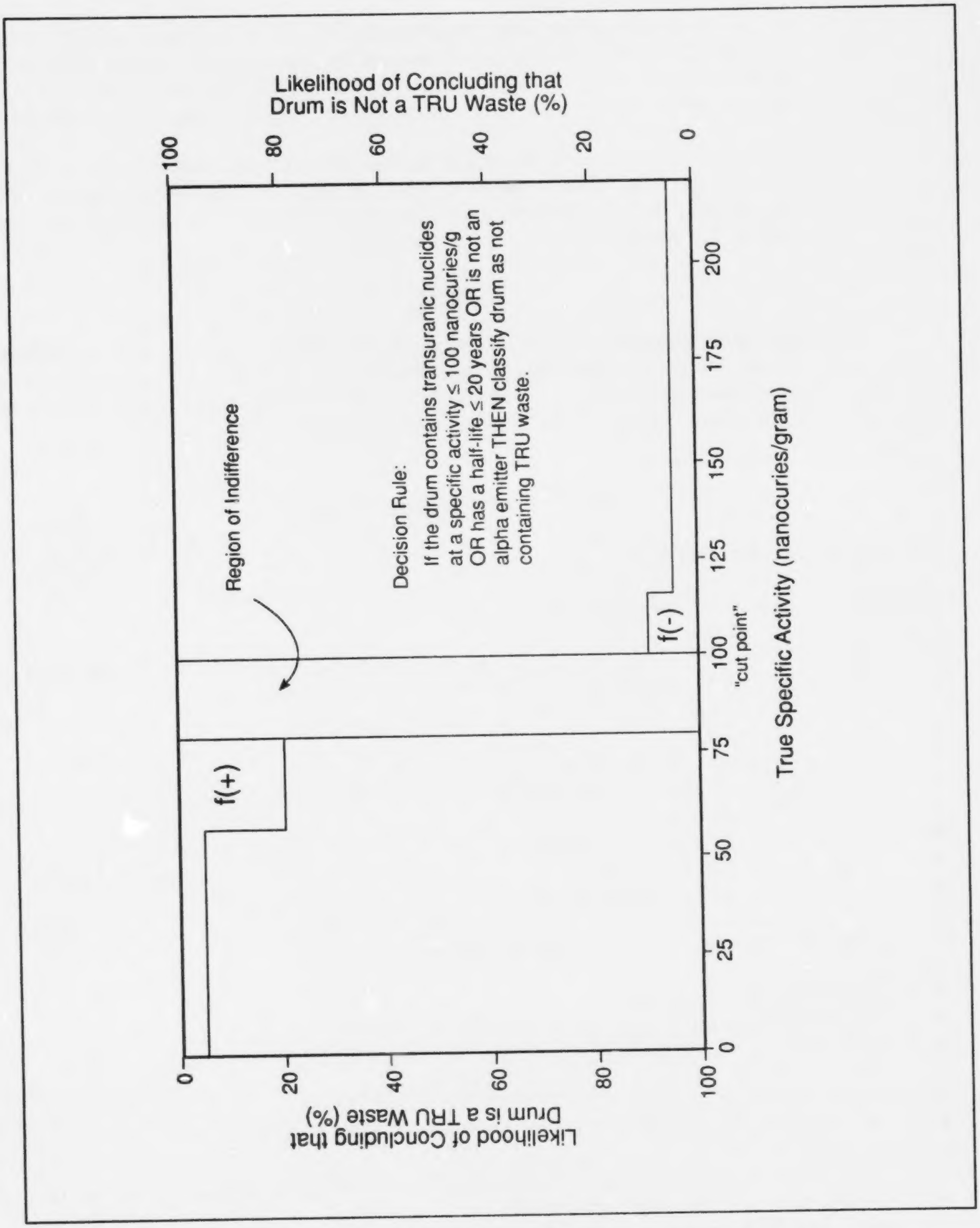
Stage 7: Optimize the Design (this stage may be considered part of the DQO process or it may be part of the Sampling and Analysis Design; the goal and output is the same in either case. The detailed discussion of study design is given in the next section of this chapter.)

Product: The lowest cost design for the study (selected from a group of alternative designs) that is expected to achieve the desired constraints on uncertainty and any practical limits.

Background: In this step, statistical techniques are used to explore and evaluate various designs for the study that meet the constraints specified in the products from the DQO process. These designs should enable the decision to be made subject to error rates no greater than those established by the uncertainty constraints within the boundaries specified for this study.

Activities: Assemble the information needed to develop alternative designs: the uncertainty constraints from the proceeding step; any budget, safety or physical constraints; cost estimates for all study activities; estimates of the natural variability for characteristics/variables to be measured; and estimates of the variability that will be introduced by the sampling and analysis process. If such information is not available, then design pilot tests to generate it, make necessary assumptions, or research improved analytical methods.

Have a statistician or someone with statistical expertise generate alternative designs and estimate the cost and anticipated error rates of each design. Select the most cost-efficient design that has acceptable performance and meets all other needs of the decision maker including political and social concerns.



Decision Rule:
If the drum contains transuranic nuclides at a specific activity ≤ 100 nanocuries/g OR has a half-life ≤ 20 years OR is not an alpha emitter THEN classify drum as not containing TRU waste.

Figure 3-4. Uncertainty limits for specific activity in drummed wastes.

If there is a reasonable possibility that natural or analytical variability will be greater than estimated or assumed, evaluate the expected performance of this design under a range of alternative conditions. Confirm that the design will yield useful results, even when conditions are more adverse than those expected or assumed.

If it appears that there is no design that will meet both the uncertainty and cost constraints, then determine whether to relax the uncertainty or other constraints, or find additional funding to achieve the desired uncertainty constraints within the specified boundaries for the study.

Example

In developing survey designs for a specific site, the planning team will need to refine and enhance the constraints in the previous steps with site-specific information to form the data quality objectives for that site. Once the decision maker and external data users understand and accept these revised constraints, the statistician will construct alternative designs that satisfy them.

Sampling and Analysis Design

Selecting the Strategy and Methods

Formulating a Detailed Site Model

Before a sampling design can be developed, the location and types of waste must be determined. This may be done as a yes/no matrix involving the following:

- Areas of interest
- Hot spots versus average values of contamination
- Surficial versus deep contamination of the waste items and the ground
- RCRA versus non-RCRA contaminants
- Radioactive versus non-radioactive
- High level of contamination
- Low level, or trace, contamination

Then the following questions are addressed:

- How is the waste emplaced?
- Are there patterns?
- Can it be segregated by type?
- What is the matrix?
- Is it layered?
- What degradation products could have been produced?

As a result of these inquiries, either a pattern can be identified upon which to base a verifiable model of the waste, or such a model cannot be developed. When such a model can be created, it forms the basis for a sampling plan in which some "representative" portion of the waste is characterized. When it cannot be created, the achievement of a high degree of certainty in the waste characterization will require opening and sampling every waste container. A very closely spaced sampling grid will be needed for a waste pile, and the project will be very costly.

An essential early part of the study will be grouping waste items into populations. A waste population may be defined on the basis of the contaminants present, the waste matrix, the level of contamination, or a process variable from the facility that generated the waste. The criterion by which the waste is divided into populations is that, in the final disposition of the waste, all of the members of a population will be treated alike.

In the example above, each waste drum was treated as a unit of a population. The project planners were sufficiently confident of homogeneity within each drum that there was no need to investigate or distinguish among the contained items. This is not always the case. Waste that has come to be co-located within a drum or a grouping of drums may be from similar populations or may be representative of many populations. The drum(s) may have been filled quickly or over a long period of time. The materials may be heterogeneous by process of generation but be from the same location.

The assumptions used to determine groupings (populations) must be well documented and tested against the needs of the project. As an example, several bags of vials may be found within a drum and initially be grouped as a population. However, the materials within the vials may be completely dissimilar chemically (by process of generation or by level of concentration), or they may all be similar by exhibiting gamma radiation but contain different nuclides. If these nuclides must be treated differently, the different bags actually represent different populations.

The sheer magnitude of the project and/or economic concerns may suggest inappropriate groupings; i.e., that all paper wastes, regardless of contamination, be grouped together. This approach should be taken only after serious consideration of the sampling objectives, addressing the questions:

- What value is added by such a grouping?
- Can the items be mixed to produce a true population (that is, can all the components be treated/disposed in the same way)?
- Is such a technique allowed by regulations (i.e., is this treatment by dilution)?
- Will a smaller number of samples be needed?

Aspects of a Preferred Sampling Design

A sampling procedure must be practical and achievable. It is easy to set conditions on the sampling procedure which appear very desirable and reasonable, yet lead to less efficient contaminant concentration estimation and decision determination. Statistically, a good estimate should have small bias and a minimum standard deviation of error. Some statistical procedures produce unbiased, minimum variance estimates as their goal (e.g., least-square regression). However, if the estimate is not required to be completely unbiased, it is often possible to obtain estimates with a smaller root-mean-square (r.m.s.) error which have small but acceptable statistical bias. With the best of intentions, a regulator might specify that the statistical sampling procedure lead to unbiased estimates (certainly a commendable property) and inadvertently force large r.m.s.

errors (relative to the given sample size) upon the estimates. These correspond to a wide confidence interval around the estimated value and poor predictability in the measured parameter.

Another desirable property of a statistical sampling plan is objectivity, as contrasted with subjectivity. An objective sampling plan obtains its estimates independently of the opinions and judgments of the project personnel. A completely objective procedure would require that prior knowledge and judgment not be used in the design of the sampling process but, instead, various random number techniques be used to select locations for sampling and other aspects of the process. If the cost per sample for collection and analysis is quite small (so that it is feasible to have large sample size), the very objective random sampling procedures are quite appropriate. Indeed, they are the popular and standard approach in market surveys and many agricultural experimental designs.

As the cost per sample for collection and analysis increases, it becomes desirable to allow some subjectivity in order to obtain the required estimate precision with a smaller sample size. This may be achieved in classical sampling theory by using stratified random sampling and, perhaps, introducing other inferred structural properties of the population. Alternatively, one may shift to methodologies such as Bayesian methods (which may require subjective estimates of prior probability functions) or the random function approach of geostatistics (which builds on an inferred spatial correlation structure within the site). Both methods use prudent, subjective judgment concerning the statistical structure of the population and the uncertainties relative to various aspects of the population to obtain greater precision from a given sample size.

In the case of a very substantial cost per sample (often true for heterogeneous wastes), the need to get as much information as possible from a very limited number of samples makes techniques such as sequential methods very appealing, since they allow the information from data collection to be used as soon as available to optimize the selection of future samples in the process. They also permit sample collection and analysis to terminate as soon as the required estimate precision or decision branch point is reached. This, in turn, minimizes the number of measurements required to attain the DQOs.

All of the above sampling schemes have areas of appropriate application. It is not a question of which is right or wrong, but rather what approach is best in a given situation. With heterogeneous wastes, the need to process many drums (or large unconfined waste piles) and the excessive cost of direct analysis are dominant aspects of the problem. An acceptable procedure has to be achievable within the limitations of money and time available, as well as being capable of implementation in such a way as to be safe to the workers involved and the public at large. An unachievable sampling/decision procedure might result in greater danger to the public than a more modest achievable procedure. This is one of the main reasons for involving technical, managerial, and administrative personnel in project scoping.

For characterizing heterogeneous wastes, maximum use of prior knowledge and non-invasive measurements should be made. If the decision can be made based on this information, further sampling may be unnecessary. If more information is needed, sequential sampling, rather than a fixed-sample-number approach, appears desirable since it allows knowledge gained at each stage to be available in the sampling at future stages. This, in turn, permits the decision process to proceed with the fewest samples and greatest dispatch and to terminate as soon as a suitable basis for the decision is obtained. The sequential approach is not popular with contracting departments because it appears much simpler to wrap up a site study in one stage. However, this approach will frequently turn out to be optimum with respect to cost, worker safety, and time requirements.

Statistical techniques potentially applicable to heterogeneous wastes are listed and evaluated in Appendix B. The statistical methodology needs to be selected carefully to obtain techniques which are most efficient in treating the special aspects of the site and the waste materials and the range of decisions/actions under consideration. No single statistical methodology can serve as a "best procedure" for all circumstances. Instead, the project planners need to consider a variety of different methods, each of which might be optimal under particular circumstances. There are also many circumstances which require some degree of further statistical research on existing methods to modify or adapt them to the special circumstances of particular waste sampling situations. Thus, it appears that professional statisticians should play an active role in many aspects of project planning.

In considering cost-efficiency, the project planners must bear in mind that waste characterization is only one of the cost elements in dealing with the site. Implementing the minimum acceptable sampling plan may not minimize the overall site remediation cost. It may be appropriate instead to perform a more rigorous waste characterization study so as to lessen the incidence of false positive results. This will result in classifying a smaller portion of the waste as exceeding the action level and requiring treatment. Depending on the expense of treatment, a substantial overall saving may be realized by expending more than the minimum required to characterize the waste.

Non-traditional Aspects of Statistical Sampling in Waste Characterization

Traditional sampling theory is concerned with collecting data that are to be used to estimate the average value of some variable of the population and to establish confidence intervals for that estimate. The characterization of heterogeneous wastes may involve additional considerations. These include the fact that the real purpose of the characterization is to facilitate the decision process in guaranteeing that relevant regulations pertaining to public safety are satisfied. Thus, the estimation of mean values of the variables is only an intermediate step to ascertaining that the proper actions are taken with a high probability.

The presence of a single "hot spot" of contamination within the waste may be much more relevant to taking the proper action than the average value of the contamination, no matter how accurately it is estimated. The location and measurement of a local maximum value within waste material is not a conventional problem within statistical sampling theory. A reasonable body of theory exists in studies of "search techniques" to locate objects of known size and shape. However, a combination of search theory with sampling theory may require further research and development before it can be applied to waste characterization in all cases.

Selecting Sampling and Measurement Procedures

Any measurement that can be made from outside the storage drum or unconfined waste pile without introducing a physical presence within the waste can be considered to be "non-invasive" or "non-intrusive." There are numerous possibilities for such measurements (see Chapter 5 for detailed discussion). These include multispectral measures of reflectance (infrared, visual, and ultraviolet bands) from satellite and aircraft flights above the site; similar observations from ground level near the waste storage; measurement of other physical properties such as temperature and radiation emitted from the waste naturally or under excitation from external sources; X-ray photographs; and such activities as a careful visual observation of the drums for markings or stamps on the drum, rust and other signs of age, and evidence of corrosion and leaking. Non-invasive techniques pose the least hazard to project workers, and they generally yield the least quantitative information about the waste. They may or may not be the least costly characterization methods.

Semi-invasive (or "minimally-invasive") techniques involve breaching the waste container or outer surface of the waste (as in a pile) but do not involve removing the waste for further testing. Therefore, these techniques usually develop information of a semi-quantitative nature that are indicative of certain characteristics of the waste. Such measurements are taken through small punctures in the waste container or waste. For instance, instruments can be lowered or driven into the waste through the bung hole in the drum.

Invasive measurements involve actually entering the waste, observing it, sorting, subsampling, and subjecting the material to direct measurements. Samples of the waste are taken and may be fully characterized by destructive means at field and permanent laboratories. During invasive testing, samples can be taken in cross section, and materials may be sorted and segregated. Normally, invasive sampling is the only source of fully quantitative and representative data. However, this technique results in an increased potential for accidental release of materials in transit and in laboratories, and may involve sample preparation processes that generate even more waste materials. It also entails the highest exposure to sampling personnel.

Exposure concerns may, in fact, dictate the selection of sampling procedures, sample size, and project phasing. If the risk is too great and cannot be mitigated by state-of-the-art technology, the project may have to be deferred until less hazardous methods have been developed, or a worst-case assumption requiring a minimal characterization study may have to be adopted. The risk of worker exposure and potential for injury must be weighted over and above cost and percent assurance of DQOs.

In considering all of the available waste characterization methods, it is recommended that maximum use of prior waste and site information be made. If this information, combined with various non-invasive measurements, is insufficient to answer the study questions, the investigators should next examine semi-invasive techniques. If these will not suffice, fully invasive sampling will be necessary. This should involve careful selection of the most cost-effective statistical procedures, preferably stepwise and sequential methods to minimize the required number of samples. The goal is to maintain safety while optimizing the accuracy of the decision process within the constraint imposed by the project budget.

Characterizing Landfills and Waste Piles

Much of the discussion herein has focused on waste stored in sealed drums. However, there are attributes of landfills and unconfined piles of stored waste that require special note. The general structure of the flowchart (Figure 3-1) and the comments in the list of statistical procedures (Appendix B) all apply here. However, the examination of the waste surface by non-invasive methods takes on a greater importance since the material is exposed, more or less, without the barrier of the metal walls of a drum. Thus, methods such as magnetic surveys, radar imagery, aerial photographs, satellite sensor imagery, electrical conductivity, etc., can all be quite appropriate, depending on the site (see Chapter 5). Historical process information should be collected as completely as possible, and a site visit is vital.

Regardless of the nature of this information, it is imperative that the unconfined waste be considered in all three dimensions, and not just over the exposed two-dimensional surface. The distribution of object sizes, types, materials, and hazard characteristics must somehow be inferred in three dimensions.

Some of the characterization decisions to be faced are: (1) What types of hazardous materials does the pile contain? (2) What methods of treatment of the material are possible? (3) Can the material be so treated and/or sealed that the site can be converted to some beneficial use? (4) If material can somehow leave the site, what are the possible pathways of migration (groundwater, atmospheric dust and debris, surface runoff)? (5) Are "hot spots" of contamination present within the unconfined waste?

The techniques of geostatistics, such as kriging and conditional simulation, and methods from biological spatial sampling, such as transect sampling, appear to be particularly appropriate for landfills and waste piles. However, many other methods, such as stratified random sampling and systematic sampling, may also be appropriate if the cost for collection and analysis of each datum is reasonably small.

One of the problems with a severely heterogeneous waste pile is that the true diversity of the materials only emerges as the samples and information are assembled. Thus, a stratification into semi-homogeneous categories is often not possible initially. Rather, it is necessary to keep a running waste classification scheme going as information is obtained. Categories are added into consideration as examples of those materials are found. Double sampling (see discussion in Appendix B) may be appropriate for these wastes. A large sample taken throughout the whole pile is collected in conjunction with a relatively inexpensive analysis scheme. This is used to establish significant categories of material and concerns. Then a smaller sample of carefully selected materials is collected and submitted to much more detailed, and expensive, analyses.

Finalizing the Project Plan

When one or several alternative study designs have been developed, they are screened according to the limitations of the project: its budget, schedule, health and safety requirements, and DQOs. If there are no designs that will be able to achieve the DQOs while satisfying the other requirements, the project planners must return to an earlier stage, revising the study design or loosening the DQOs (this must, of course, be done in consultation with the decision-maker). When more than one design meets the requirements, one design is chosen for implementation. This choice is usually based on cost considerations, but other factors may be of greater importance. For example, there may be pressure to complete the study as quickly as possible, or the project team may wish to implement a statistical design they are familiar with, rather than one that would be experimental in their application.

The final step is the preparation of the project planning documents. These generally include a sampling and analysis plan, a set of operating procedures, a QA project plan, a health and safety plan, and the overall project workplan. There may not be standard procedures for the non-invasive imaging techniques or the sample collection activities of the heterogeneous waste study. Innovative QA methods may be called for, and the need for frequent on-site corrective actions can be anticipated. Consequently the common practice of borrowing boilerplate planning documents from previous studies is unlikely to be technically sound. Those preparing the planning documents and those who will be responsible for reviewing them should budget ample time for this stage.

Conclusions

Recognizing the imperative need for careful concern for the health and safety of the public and the workers involved in the waste characterization activities, it is important that characterization, remediation, and monitoring procedures be selected which are achievable with the available resources of manpower and budget. It is also important to evaluate the long-term consequences of "no action" along with the various possible remedial actions, since "no action" may have worse public safety effects than other feasible, but perhaps not ideal, solutions.

A general course of action for heterogeneous waste characterization is recommended. This consists of three major stages: (1) The first stage entails the project scoping, definition of data quality objectives and project decision choices, the collection of historical and non-invasive measurements, and a review to see if sufficient information is available for a decision at this point. (2) If not, the project team proceeds to examine the relevant and appropriate statistical methodologies, and to select the one or several choices which are both cost-effective and incorporate sufficient safety. (3) The last stage of the waste characterization study involves actual sampling (first, with cautious semi-invasive measurements, and then, if that is not sufficient for a decision, with fully invasive sampling). In the actual sampling, a pilot sample is recommended first as a guide for planning the future cycles of more complete data measurements. These cycles of sample collection and analysis are alternated with review and interpretation until enough information is obtained for making the appropriate action choice.

Recommendations

There are two actions that regulatory agencies could take to improve the quality of environmental studies by influencing the process of study planning and DQO establishment. One would target project managers, the other decision makers.

Technical project managers are sorely in need of guidance for setting appropriate and workable confidence intervals for environmental data. All of the sources of variability included in population and measurement error need elucidation. DQOs are currently set according to rules of thumb that vary across the country and among organizations. To ground their studies on a firm technical base, project managers need more than these arbitrary rules of thumb, and the regulated community deserves more. A detailed compilation of the courses taken in past studies could help project planners select reasonable DQOs early in their own projects, obviating the need for repeated sampling and revision of goals. Such a compilation should be broken down according to the medium to be characterized: air, water, soil, heterogeneous waste, and homogeneous waste (industrial sludge, for example). For each medium, a number of past studies should be detailed. The text should concentrate on the data quality objectives: what they were; on what basis they were established; whether they were achieved; if not, why not; and the quality of data that was generated. A simple synopsis of this type, detailing what has worked for different site conditions and what has not, would be a great help to study planners. Unfortunately, it is likely that little information is available for studies characterizing heterogeneous wastes based on numerical DQCs.

A similar synopsis would be useful for decision makers. In this case, the description of each past study would focus on the uncertainty of the decision(s) that were to be made. The study description would detail the uncertainty constraints associated with the decision to be made: the acceptable frequencies of false positive and false negative decision errors that were designated and the region of indifference for the decision (see Figure 3-4). This document would be helpful in two ways:

- it would provide decision makers with information on what levels of certainty are achievable for various types of decisions concerning a range of media and contaminants, and
- it would provide a national information base that could be used by EPA officials to establish uniform guidelines for making cleanup decisions.

It must be emphasized that these documents would not alleviate the need for incisive, site-specific planning as each study is initiated.

Project managers would benefit greatly from the development of analytical and software tools to aid in the planning process for characterization studies. Optimizing the study design and scoping a study that is within budget yet achieves the DQOs is an iterative and frequently a very tedious process. This process could be expedited with the help of computer programs to allow quick alterations of project design and comparisons among designs. Such programs could perhaps be based on existing software for accounting or cost-benefit analyses. Alternatively, new software could be developed based on a gaming approach or a systems approach. A general, master program or expert system could be adapted to be quite specific to the needs and constraints of particular types of projects. It must be emphasized that no "cookbook" will ever be available for this exercise: difficult-to-quantify factors such as worker safety and professional judgment will always play an important role. But it would be very worthwhile to adapt or develop tools to assess and compare the quantitative aspects of study design.

Appendix B, which is a supplement to this chapter, summarizes a number of statistical methods that might be useful in some of the circumstances of heterogeneous waste characterization and gives a partial evaluation of the applicabilities of the methods. It is clear from this summary that there is a need for a very detailed handbook to evaluate in depth each of the methods for its appropriateness in waste characterization, and to provide examples and guidance to users as to the best choices in particular situations. Enough experience has been accumulated in waste characterization and in the application of alternative statistical techniques that an initial version of such a handbook could be assembled now. The handbook would be expected to evolve over time and would require the efforts of many contributors.

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Chapter 4

QA/QC and Data Quality Assessment

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Introduction

Quality assurance, quality assessment, and quality control are important for any study. The sampling of heterogeneous waste makes these study elements even more important because of the variability in the sampled material and the need to determine whether the data from a sampling effort accurately represent that material. Sources of variability in the measurement process, which can obscure the detection of natural spatial and temporal trends in the sampled material, can be increased in the sampling of heterogeneous material. Those sources of variability have been identified previously in "A Rationale for the Assessment of Errors in the Sampling of Soils" (1), and they occur in the collection, transportation and handling, preparation, sub-sampling, and analysis of the sample. The challenge for the investigator is to determine whether the bias and variability introduced during those phases of a study are sufficiently small, in relationship to the natural spatial and temporal variability of the sampled material, that they may be neglected. Quality assurance, quality assessment, and quality control are meant to aid the investigator in meeting this challenge.

The terms quality assurance, quality assessment, and quality control are often misunderstood (see definitions, Chapter 2). Activities associated with these terms are often viewed as burdensome requirements that drain resources from an investigation and slow its progress. Some people view their completion of a Quality Assurance (QA) plan as representing their total commitment to QA when in fact it only represents the beginning. Definition of the data quality objectives (DQOs) may be attempted in a rigorous fashion, if it is done at all, but ascertainment of whether those objectives have been met usually proves to be difficult. All too often ascertainment of whether the DQOs were met, or whether they were appropriately chosen, is never completed.

It cannot be emphasized too strongly that the application of up-front, sound quality assurance procedures and documentation is the most important element for continuity, reliability, and confidence in the waste investigation project. Applied reiterative quality assurance provides for maximum utilization of resources and ultimate economy of operations. It is the best way to avoid having to repeat a job at an increased cost.

There are two important conditions for successful application of QA to achieve project goals. First, the support of QA must come from the top down and permeate the way an agency or program acts in its usual and accustomed way of doing business. QA must be supported throughout the entire management and production structure of the organization generating the data. QA practices and procedures must start with the inception of a problem-solving design and be a cooperative effort of all involved parties. This is accomplished through established and accepted guidance and standard operating procedures, implemented even in the initial scoping phase of project definition. Second, QA must be recognized and implemented as a reiterative and plastic process. By so doing, all parties to the study have an opportunity to apply their areas of specialty or expertise. Especially as concerns heterogeneous materials, QA must be an ongoing process, evolving as problems are encountered and solved during the waste study.

General guidance for QA/QC in hazardous-waste investigations is provided by EPA (2,3,4,5). This chapter attempts to lay out a basis for QA/QC in the sampling of heterogeneous waste. The intention is not to duplicate standard guidance on the subject; rather, the purpose of this chapter is to translate some of the standard QA/QC requirements and procedures into an area where QA/QC can be most difficult to incorporate - sampling of heterogeneous waste.

Standard guidance and protocols for QA fall short when applied to heterogeneous materials. In attempting to ensure and evaluate data quality, the study planner frequently discovers that:

- there are no applicable standard reference materials for insertion into the sample train;
- there are no standard methods for necessary field and laboratory activities;
- data representativeness, precision, and accuracy are difficult to assess with standard techniques;
- those who audit project activities are unfamiliar with the procedures used and can neither evaluate the appropriateness of those procedures nor offer corrective guidance.

Some of these issues, or portions of all of them, are beyond the current state of the art for heterogeneous waste characterization procedures. For those that can be addressed, two scenarios are presented herein to focus discussion on the sampling of heterogeneous waste. One is the sampling of waste piles with a variety of wastes, in a variety of forms, and in a variety of sizes. The other scenario is the sampling of drums in which the materials were intended to be isolated from the environment and from human observation and contact. The application of QA/QC to both of these scenarios is important, but different adaptations have to be made to reflect the different nature of the problems.

Two questions commonly asked in a QA/QC program are:

- How many, and what type, of quality assessment samples are required to assess the quality of data in a field sampling effort?
- How can the information from the quality assessment samples be used to identify sources of error and uncertainties in the measurement process?

Suggested methods to address these two questions are provided in EPA (1), particularly for the sampling of soils. Some adaptations may be made for other media and other situations. The following discussion draws upon the rationale in EPA (1) for the sampling of heterogeneous waste and the assessment of data quality.

The approach described herein is based on the statistics of a normal distribution. Hazardous-chemical or radionuclide data from the sampling of heterogeneous wastes are unlikely to follow a normal distribution. As discussed in the chapter on study planning, before using any statistical model, the investigator must establish what the true distribution is. If a transformation can bring the concentration data into a normal distribution, the approach described in EPA (1) may be used to assess, and potentially control, sources of bias and variability throughout much of the sample collection and measurement process. Sampling of heterogeneous wastes will probably require some modification of the approach, particularly when sampling involves remote sensing methods or barrels of assorted waste. Suggestions are provided on how these situations may be approached.

QA/QC in Sampling Heterogeneous Waste

Sampling involves many different steps and techniques. The general approach in QA/QC is to examine those steps and techniques in a rigorous fashion to determine the bias and variability and whether the data associated with the routine sampling meet the DQOs. A variety of tools are available including audits, education, documentation, and a variety of standard materials, procedures, and methods. QA/QC for heterogeneous waste sampling is especially difficult because of the paucity of standard materials, procedures, and methods. Sound QA theory suggests that new categorization and quantification techniques should be developed for heterogeneous hazardous waste sites.

An initial question to consider is whether there are available standard materials, procedures, and methods that are appropriate for the questions that one seeks to answer in the sampling activity. The DQO process and the available sampling strategies and methods which may be employed have been discussed in previous chapters. Unfortunately, a poor sampling plan and inappropriate DQOs can have profound impacts on a QA/QC program. For example, in characterizing the contents of a drum, many approaches may be taken depending on the overall objectives of the characterization. If the objective is to determine whether the drum may be transported by common carrier to another location, then particular emphasis will be given to determining whether the contents and packaging are in conformity with DOT regulations. Alternatively, if the objective is to determine whether the drum may be stored in a particular location for a long period of time, the form and substance of the contents of the drum may have to be determined, especially if failure of the drum could lead to significant risk to human health and the environment. Measurements of the drum under those two scenarios would employ different monitoring methods, have different DQOs, and carry different levels of QA/QC. The level of QA/QC should be based upon the degree of confidence required in knowing whether the data meet the DQOs and in being able to report the QA/QC data accurately. Until the DQOs have been specified and sampling and analytical methods have been selected, a QA/QC program for heterogeneous materials cannot be prescribed, and major impediments to the implementation of the QA/QC program cannot be addressed.

How does one employ QA/QC in the characterization of waste in a drum? If a conventional method such as GC/MS is employed to analyze samples from the drum, then the analytical QA/QC may be conventional. QA/QC in the laboratory can be the same as that used for the sampling of other, more conventional media. Assessment of variability and bias in the steps leading to the analytical step remains an issue. Alternatively, if a field physical method such as a neutron assay method is used, then new QA/QC methods may need to be developed and validated. In this instance, QA/QC for a remote sensing method would likely include the sampling and analytical steps because they are more closely intertwined. Common to both measurement methods is the question of the number and timing of observations that are needed to assess the performance of the measurement methods. Also common to both methods is the question of whether the "truth" can be ascertained. If the reported parameters are a function of the measurement method, there can be problems in ascertaining the "truth." Depending on the objectives of the study, it may not be necessary to know the "truth," e.g., the absolute concentration of a substance in the drummed wastes, to a high degree of accuracy and precision. If no standards are available for assessing bias and variability at various steps in the sampling of heteregeneous materials, then the QA/QC can be complicated and more severely restricted. Application of QA/QC to characterization of heterogeneous wastes requires careful thought.

Assessment of Bias and Variability

Systematic errors, termed bias (B), can be introduced at many points in the waste characterization process (Table 4-1). Bias causes the mean value of the sample data to be either consistently higher or consistently lower than the "true" mean value. Bias may result from faults in sampling design, sampling procedure, sample preparation, analytical procedure, contamination, losses, interactions with containers, deteriorations, displacement of phase or chemical equilibria, and inaccurate instrument calibrations. When the sampled material is heterogeneous, subsampling that favors one type of item over another is an obvious potential source of bias. Laboratories usually introduce various quality control samples into their sample load to detect possible bias. Bias in the sampling of heterogeneous materials is difficult to detect. Components of bias can be discovered by the technique described as standard additions or by using evaluation samples. On the other hand, it is difficult to demonstrate that bias is not present because an apparent lack of bias may be the result of an inability to measure it rather than its actual absence.

Variability in the data can come from bias that changes over time, from natural variability, differences between batches, or from imprecision in the collection, handling, transportation, preparation, sub-sampling, and analysis of the sample (Table 4-2). Also, variability occurs in the measurement process from the heterogeneity of the material and random errors throughout the measurement process. The variability caused by any type of random error is frequently described quantitatively by the variance, σ^2, of the random error, or by the positive square root, the standard deviation, σ, of the random error. The variances of independent random errors are additive in that the variance of the sum of errors is the sum of the variances of the individual errors (Table 4-2). Other quantifications of variability do not have this useful, additive property.

Separating the different components of error requires proper selection, use, and timing of QA/QC samples throughout the study. A rule of thumb is that the more observations that are made, the greater the degree of confidence that may be placed in the observations.

Table 4-1. Elements of measurement bias in environmental sampling

B_s = Measurement bias introduced in sample collection not caused by contamination
B_{sc} = Measurement bias introduced in sample collection caused by contamination
B_h = Measurement bias introduced in handling and preparation not caused by contamination
B_{hc} = Measurement bias introduced in handling and preparation caused by contamination
B_{ss} = Measurement bias introduced in sub-sampling not caused by contamination
B_{ssc} = Measurement bias introduced in sub-sampling caused by contamination
B_a = Measurement bias introduced in the laboratory analytical process not caused by contamination
B_{ac} = Measurement bias introduced in the laboratory analytical process caused by contamination
B_m = Total measurement bias (sum of the above components)

NOTE: Biases, other than contamination biases in the measurement of a sample, are often dependent on the original concentration of the contaminant being measured and on the sample matrix. Biases caused by contamination are listed separately because some QA samples, such as rinsate samples, detect only contamination bias.

Table 4-2. Elements of variability in environmental data

$$\sigma_t^2 = \sigma_m^2 + \sigma_p^2$$

where σ_t^2 = total variability

σ_m^2 = measurement variability

σ_p^2 = population variability

$$\sigma_m^2 = \sigma_s^2 + \sigma_h^2 + \sigma_{ss}^2 + \sigma_a^2 + \sigma_b^2$$

where σ_s = sampling variability (standard deviation)

σ_h = handling, transportation and preparation variability

σ_{ss} = sub-sampling variability

σ_a = laboratory analytical variability

σ_b = between batch variability

In the scenario of characterizing heterogeneous waste in a drum, analysis of the drum could involve the collection of one sample from the drum and its extraction and analysis by GC/MS. Experience would suggest initially that QA/QC for the sample in the laboratory would be relatively easy because of previous experiences, practices, and the ready-availability of standard materials for the GC/MS in the laboratory. More experience would suggest that the variability and biases in the laboratory measurement are likely to be minor in comparison to the variability and biases involved in collection of the one sample. Conventional statistics suggest that one sampling of the drum of heterogeneous wastes would be inadequate and that some statistics-based approach would be needed for increasing our confidence that our sample collection is representative of the contents of the drum. The bias and variability associated with the GC/MS analysis of the sample may be on the order of 20%, while the act of collecting the sample could result in orders of magnitude differences in the reported values depending on where and how the contaminant was physically sampled within the heterogeneous mixture. In many QA/QC programs, a great deal of resources and attention are devoted to the laboratory analysis when greater attention should be given to earlier phases of the sample collection process.

If a drum is sampled by a remote sensing method, assessment of bias and variability becomes more complicated. Bias may be represented in terms that are related to other remote sensing methods or to more conventional analytical methods. The DQOs should be useful in determining how bias should be reported and assessed. As in the sampling of a drum for GC/MS analysis, the process of making the measurement can introduce more bias and variability than the analytical process itself. Variability is more readily assessed, but bias becomes more complicated when known concentrations of contaminants in a sample matrix similar to that of the routine samples may not exist. Whenever possible, known materials with known concentrations of contaminants that are indistinguishable to the operator of the analytical test method should be analyzed to help determine bias and variability of the test method. Duplicate measurements may be made to assess variability, and calibration standards may be used to assess and control bias within the measurement method, but double-blind materials are preferred for assessment of cumulative bias and variability at the various stages of the measurement process.

QA/QC Samples

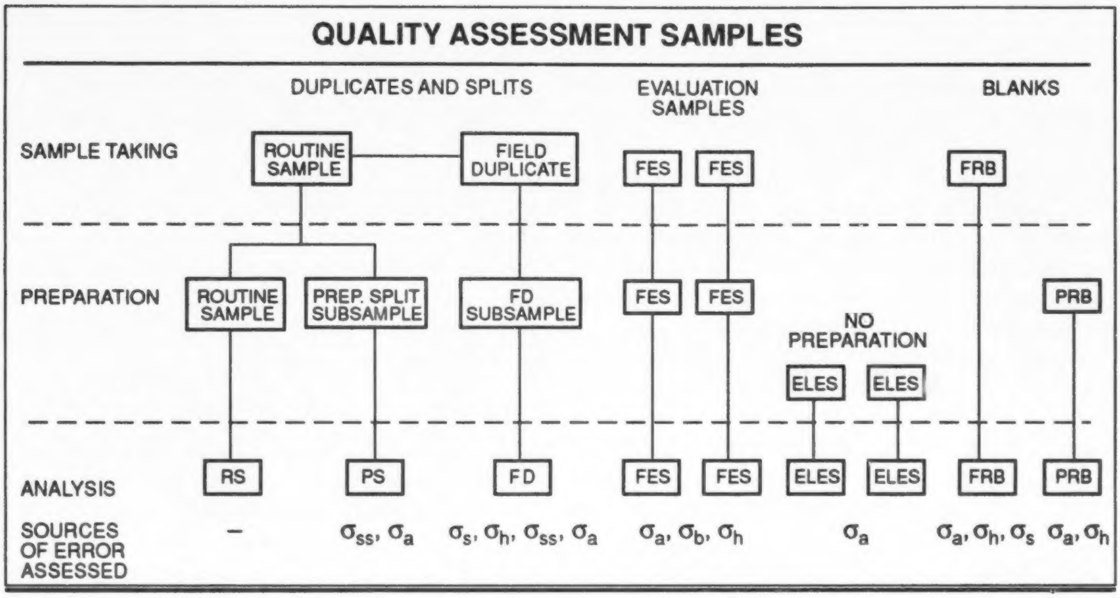
One important tool, defined and described in more detail in EPA (1), is a suitable "reference material" to assess bias and variability. "Reference materials" may be described as materials having a known concentration, or property, that is relatively stable over time. "Standard reference materials" are defined as being materials produced by the National Institute of Standards and Technology. Other terms may be used to define and describe reference materials. These materials are most often thought of, in terms of laboratory measurements, as well-characterized, relatively homogeneous materials in small quantities that are usually used to assess bias and, alternatively, precision of a method. These samples may not be appropriate for the characterization of heterogeneous waste. For less orthodox, relatively new methods such as the physical imaging of drum contents, there are apt to be few, if any, reference materials that are suitable. When inadequate reference materials exist, some consideration needs to be given to their manufacture. The difficulty, cost, and time involved in making up the materials may not be appropriate for a particular investigation. The decision to make up these materials depends, in part, on the objectives of the study and the degree of confidence that is needed in the results from the QA/QC program.

A relatively new practice, and an especially important one in assessing QA throughout the sample-collection and measurement process, is the preparation of site-specific performance evaluation (PE) materials. These materials should be double-blind in that they cannot be readily recognized, and their established properties are unknown to the analyst. They offer the advantage of being able to accurately assess the performance of a measurement process through the use of natural materials that closely resemble native materials under similar conditions. They may be made from the same materials that are being routinely sampled. While site-specific performance evaluation materials offer opportunities for obtaining unbiased estimates of bias and variability throughout the sample collection and measurement process, they are not used often, in part because established procedures do not exist for their use and for their fabrication.

Site-specific performance evaluation materials for characterizing heterogeneous materials may be made by spiking uncontaminated waste materials with a known concentration of contaminant or surrogate. Site-specific performance materials for the characterization of a drum by field physical methods would at first appear to be less straight-forward, but may actually be easier. Under the scenario of the drum that is being examined by a physical method, a site-specific performance evaluation material could be made by packing a drum with items of known properties. For example, gloves, containers of liquid hazardous waste, and debris could be inventoried and packed into a drum for analysis by others. This drum could be introduced into the routine sampling stream and could be classified as a "double-blind." This "double-blind" sample would yield valuable data on the performance of the measurement system if the drum were analyzed just once, or if the drum were randomly reintroduced into the sampling stream several times over the course of the study.

Other QA/QC samples, such as blanks, are described in EPA (1). While that document focused on soil sampling, these QA/QC samples may be used, with adaptation, for other media and other situations.

One of the most powerful tools available for QA/QC purposes is the concept of replicate, duplicate and co-located analyses. They are particularly important for the sampling of heterogeneous waste because of the large spatial and temporal variability associated with these wastes. Separation of natural spatial and temporal variability in the sampled material from variability and bias in the measurement process may be achieved by the use of co-located, replicate and split samples at various points in the sample collection and measurement process. Creating a co-located sample in the sampling of a waste pile would entail the sampling personnel moving a very short distance from where a routine sample was collected to collect another sample. The co-located sample would be identified and treated as a routine sample. (The co-located sample is sometimes known as a "field duplicate.") If the variation within the pile (the sample population) is very great, the decision maker will be alerted to this by the disparate results for the routine and co-located samples. Prior to its receipt at the analytical instrument, a sample may be split. (The split samples may be known as "preparation splits.") At the instrument, replicate or duplicate observations may be made to assess variability in the use and operation of the analytical instrument. All of these samples and procedures can assess variability from a variety of sources at various times. The information from these samples can be used to determine whether the variability in the measurement process is so large that it needs to be controlled or is sufficiently small that it only needs to be reported. Figure 4-1 is a schematic of how QA/QC samples may be used to identify various sources of variability and bias. Details on the computation of variability from the QA sample data are given by EPA (1).


QUALITY ASSESSMENT SAMPLES
DUPLICATES AND SPLITS
EVALUATION SAMPLES
BLANKS
SAMPLE TAKING
ROUTINE SAMPLE
FIELD DUPLICATE
FES
FES
FRB
PREPARATION
ROUTINE SAMPLE
PREP. SPLIT SUBSAMPLE
FD SUBSAMPLE
FES
FES
NO PREPARATION
ELES
ELES
PRB
ANALYSIS
RS
PS
FD
FES
FES
ELES
ELES
FRB
PRB
SOURCES OF ERROR ASSESSED
–
σ_{ss}, σ_a
$\sigma_s, \sigma_h, \sigma_{ss}, \sigma_a$
$\sigma_a, \sigma_b, \sigma_h$
σ_a
$\sigma_a, \sigma_h, \sigma_s$
σ_a, σ_h

Types of Samples	Description
Field Evaluation (FES)	Samples of known concentration are introduced in the field as early as possible to check for measurement bias and to estimate precision.
Low Level Field Evaluation (LLFES)	Low concentration FES samples check for contamination in sampling, transport, analysis, detection limit.
External Laboratory Evaluation (ELES)	Similar to FES but without exposure in the field, ELES can measure laboratory bias and, if used in duplicate, precision.
Field Matrix Spikes (FMS)	Routine samples spiked with the analytes of interest in the field check recovery and reproducibility over batches.
Field Duplicates (FD)	Second samples taken near routine samples check for variability at all steps except batch.
Preparation Splits (PS)	Subsample splits are made after homogenization and are used to estimate error occuring in the subsampling and analytical steps of the process.
Field Rinsate Blanks (FRB)	Samples obtained by rinsing the decontaminated sampling equipment with deionized water to check for contamination.
Preparation Rinsate Blank (PRB)	Samples obtained by rinsing the blank sample preparation apparatus with deionized water to check for contamination.
Trip Blanks (TB)	Used for Volatile Organic Compounds (VOC), containers filled with American Society for Testing and Materials Type II water are kept with routine samples through the sampling, shipment, and analysis phases. Other types of trip blanks can be created.

Samples may be submitted non-blind, single-blind, or double-blind, as required for data evaluation. See Table 4-2 for definitions of sources of error.

Figure 4-1. Quality Assessment Samples

Even when unconventional characterization methods are employed, the use of duplicate measurements is important. A drum could be analyzed by the same instrument and same operator consecutively or over a period of time. The drum could be analyzed by the same instrument at different times by different operators to examine the variability associated with the different operators. Alternatively, the drum could be examined by two modifications of a basic physical method to determine the sensitivity of the reported data to a particular method. The choice and use of a particular duplicate or replicate sampling approach depends on the overall data quality objectives and the degree of confidence that is needed in knowing the source and magnitude of variability and bias throughout the sample collection and measurement process. Pertinent estimates of variability may also be available from previous studies.

How Many Observations or Samples are Needed?

Several answers can be provided to this question. The precise answer depends on historical data from previous studies in which QA/QC was employed to assess bias and variability throughout the sample collection and measurement process. The precise answer also depends on the Data Quality Objectives and on the measurement quality objectives (MQOs). The distinction between DQOs and MQOs is important and requires explanation.

Data Quality Objectives are intended to cover an entire study, but most often emphasis is given to the measurement phase of the investigation. Precision, accuracy, representativeness, completeness, and comparability are terms used in setting DQOs and are usually addressed in terms of the analytical portion of an investigation. Decision-makers must be concerned with the larger aspects of these terms, however. For example, a decision-maker may want to know whether the reported data are accurate to within 20% of the true value. This QA/QC parameter might be important in considering the action to be taken in relationship to an established action level. The data quality objective for accuracy includes the method by which the sample was collected and how accurately the collected sample measures the contaminant in an area. A data quality objective for accuracy may not be appropriate for the analytical phases of an investigation, e.g., the MQO for accuracy, since biases and variabilities outside the analytical portion of an investigation are included.

MQOs are meant to apply to the analytical phases of an investigation. Terms for precision, accuracy, representativeness, completeness, and comparability are more readily appreciated when applied to the analytical phase of an investigation. The distinction between DQOs and MQOs is important because observations, i.e., samples, are taken in a QA/QC effort to determine whether these objectives are being met.

The question remains, then, how many samples are needed? If historical data indicate that inaccuracy or variability is increased in the preparation and handling of a sample, and this affects detrimentally the accuracy needed to meet the MQOs, then more frequent sampling of this portion of the measurement process is justified. As another example, assume that the values reported are near the action level; bias is particularly important in meeting the DQO for accuracy, and the consequences in knowing whether a population of waste is above or below that action level are great. In this case, greater attention may need to be devoted to the sample-collection step and to the use of field duplicates to assess the variability. The number of samples required depends on the available resources, the required degree of confidence, and the objectives of the study.

The EPA (1) provides tables and a discussion for the number of samples that are required to obtain a certain level of confidence when the data are normally distributed or can be transformed to the normal distribution. The precision of an estimate, s^2, of the "true" variance, σ^2, depends on the number of degrees of freedom for the estimate which is directly related to the number of quality assessment samples. Statistics texts contain tables that give the confidence intervals for various degrees of freedom, based on an assumption that the data are, or have been transformed to, normally distributed data.

Equations are provided in EPA (1) for assessing the errors in the sampling of soils, and these may be applied to more heterogeneous materials. The equations and tables in EPA (1) are also incorporated into the public-domain computer program ASSESS (available from EMSL-LV). This program resembles a computer-based spreadsheet, and computes measurement errors, provided enough QA/QC samples of the right type have been taken throughout the study. ASSESS indicates when insufficient samples exist and certain variabilities cannot be computed.

ASSESS can display graphically the degrees of confidence that exist for the measurement of variability in the individual portions of a study. Certain portions of the study receive more QA and QC than other phases. For those portions of the study that are monitored to a high degree, the variability may be low and ignored, or the variability may be high and may need to be addressed. For those portions of the study that are not monitored to a high degree, the variability may be low, but more QA/QC samples may be required, or the variability may be high and more QA/QC samples may be required before potentially difficult and expensive corrections are taken.

If the study is complete, the reported measurements from a QA/QC program can be termed as quality assessments. The quality assessment data are reported along with the routine sample data to provide the decision-maker with a measure of the quality of data available for making the decision. The form in which the QA results are reported is crucial. Tables of numbers buried within voluminous data appendices are of little use to decision-makers. Instead, the results should be presented in simple tabular form and interpreted in the text of the report. What is the variability of each stage of the sampling/analysis process, and what does it mean for interpretation of the routine sample data? Based on this information, the decision-maker may choose to initiate another phase of sampling and characterization.

Research Recommendations

If quality assurance is the process of "demonstrating we are doing the right thing," and quality control is the process of "demonstrating we are doing things right," then it becomes obvious that existing QA/QC procedures must be adapted to deal with unconventional waste characterization problems. Quality assurance, as discussed here, is a process that starts with the initial planning of site operations. The majority of problems in both QA and QC relate to the question of representativeness of the sample data to the actual conditions of the site; these problems are especially acute with heterogeneous wastes. For site managers who must have confidence in the data they use for decisions, the credibility of the data is proportional to the degree of representativeness that can be documented or demonstrated.

The following QA/QC research needs address the concerns expressed by professionals from a number of disciplines who are involved in operations at heterogeneous hazardous waste sites. The first set of research needs is concerned with the Data Quality Objective process and its dependence on statistical methods in formulating the DQO(s). When the generally used "status quo" statistics are overwhelmed by the variety and complexity of a heterogeneous waste site, alternative planning tools are needed. These should include:

- A model (or criteria for a model) to warn the project team that conventional approaches are either failing or inflating the proposed project beyond reasonable or acceptable levels of time, money, or litigational potential. This model would be one component of the broader project-planning tools recommended in the previous chapter.
- An interdisciplinary checklist of statistical terms and definitions appropriate to DQO applications.

The second set of research needs involves the quality control aspects of operations at heterogeneous waste sites. Areas that need development include:

- Field attainable quality control sampling methodologies. Methods should be defined and described to permit repeatable, practical samples to be taken with some confidence that the reported data are representative and accurate for the sampled material. Standardization of sample collection methods (wipe tests, physical parameter measurement procedures, etc.) is essential for the larger scale debris and containerized waste problems.
- Sampling methodologies that can deal with the problems of particle size and multiphase matrices. These may include some bulk extraction techniques that would effectively start the analytical process in the field. These recommendations are expanded upon in the following chapter; they are mentioned here because the availability of reliable methods for generating representative samples is very much a QA issue.
- The techniques of manipulation, preparation, and packaging of site specific materials. These are needed to provide reference materials for performance evaluation.

Many of these research or development efforts may be accelerated if they are conducted in conjunction with ongoing site investigations rather than in isolated settings. The following measures are strongly recommended:

- Developers of new methodologies and procedures should document their applications as completely as needed to assure timely and adequate training of end users of the products.
- Practical trials, both laboratory and field, should be performed in the presence of experienced field personnel and active, qualified Quality Assurance staff that will be expected to audit the actual use of the new method at different sites.
- Parallel development of applied technologies should be encouraged and utilized wherever possible, e.g., the development of bulk quantities of reference materials for treatability studies as a preparatory step in the development of PE materials.

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Chapter 5

Sample Acquisition

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Introduction

This chapter presents procedures for sampling and characterizing heterogeneous hazardous wastes. The chapter deals with both uncontained wastes consisting of landfills and piles and contained wastes such as drums and boxes. Unfortunately, there is relatively little guidance available for landfill sampling beyond the standard site characterization and soil and waste sampling techniques. Landfilled waste is seldom characterized due to the difficulty of obtaining representative samples and the hazards of invasive sampling. The problems of sampling semi-homogeneous waste in containers have been addressed by EPA in other documents (1,2,3). This chapter concentrates on characterization of extremely heterogeneous contained wastes and relies on the experience of DOE and its contractors for characterization of radioactive and mixed wastes.

Sampling and characterization of heterogeneous hazardous waste pose several major problems, including obtaining representative information and assuring personnel safety. For these reasons, relatively few landfills have been intrusively sampled and very little literature exists on managing the unique problems of extremely heterogeneous waste. Landfills of relatively homogeneous materials or of known content have been sampled using conventional technologies. In other cases, unique approaches have been developed. Current EPA guidance on studying municipal landfills that are NPL sites recommends against detailed waste characterization, unless discrete, accessible "hot spots" of contamination have been identified (4).

Before embarking on the sampling of hazardous wastes in landfills, piles, or containers, it is prudent to obtain all relevant information that may permit achieving the objective without actually sampling (see Chapter 3). It is also prudent to scrutinize the initially-defined project objectives and approaches critically on the basis of the sampling problems, hazards, and potential costs. For example, it may be possible to consider a landfill as a black box, characterize the area around the waste remotely, and sample contaminants leaving the site via air, leachate, groundwater, and biota, rather than intrusively sample the waste. The same approach holds for drum and container sampling. Remote interrogation can provide some but not all information about the contained waste. Constructive negotiation between the regulators and the regulated party should be part of the DQO process. This will allow the parties to avoid spending huge sums and committing large staffs to sampling and characterization projects that yield little benefit.

Characterization of Uncontained Heterogeneous Wastes

General Considerations

With the increasing number of landfill facilities on the NPL, investigating landfills for evaluation of source control measures and removal alternatives is becoming increasingly important. Conditions at each landfill are unique and require detailed site-specific investigations into their structure and the nature of the solid and liquid wastes contained within each system. The hazardous and radioactive wastes present in the landfill can coexist in multiple phases (i.e., gas, liquid, pure solid, or adsorbed to solids). The material can be containerized or uncontained.

Sample acquisition from a landfill can be very costly, labor intensive, and dangerous. The deposition of debris on the site poses difficult problems for those attempting to collect "representative" samples of the site. The problems include, but are not limited to:

- What is representative? When faced with a collection of materials of assorted sizes, types, and contaminants in various phases, all arranged in unpredictable distributions over a large area (several acres), one can begin to realize the difficulty of collecting a sample that is truly representative of the entire site.
- How does one characterize the health risks of large entities (e.g., a refrigerator)? Large objects other than white goods may be ground to manageable sizes. However, the contamination may be associated with only the surface of the object. Grinding would cause undue dilution either by volatile losses or by combining interior uncontaminated material with surface contaminated material. Wipe tests have been used on surfaces, but currently no agreed-upon action limits in units of concentration per surface area are available.
- Should the objects be sorted into populations by size, material type, or suspected contamination? Without *a priori* knowledge of the contents (e.g., percentages of paper, metallic objects, plastics, etc.) and the contaminants present (e.g., heavy metals, volatile organics, semivolatile organics, etc.) in a given landfill, it is difficult to selectively sort the material to obtain an estimate of the distribution of contaminants.

A landfill can also be characterized by remote sensing coupled with indirect measurements, that is, sampling of environmental media rather than the waste itself. Landfill waste sampling is usually undertaken as a last resort and primarily for remedial purposes. When waste sampling is called for, it is highly site-specific. Indirect sampling is preferred for several reasons, the most important being protection of worker health and safety.

Indirect Characterization Techniques

In sampling heterogeneous wastes in a landfill, there are two requirements that at first glance appear to be diametrically opposed. The first is to obtain sufficiently large samples to encompass all the types and sizes of materials representative of each portion of the entire site. The second is to obtain sufficiently small samples that they can be handled by the analytical laboratory.

Theoretically, the largest sample that could be taken would be the entire landfill site. This, of course, is impracticable. However, a landfill can be approached as a black box. The reactions, behavior, and mobility of the contents of the black box can be ascertained by monitoring the effluents or emissions from the system. Monitoring the input and output from the black box may serve as a means of obtaining the largest possible sample that is representative of the entire site. However, the investigator must keep in mind that landfills are dynamic systems which can take more than 30 years after filling is completed to reach an equilibrium, where infiltration through the landfill cover equals leachate (5).

Leachate Monitoring

Monitoring of regulated landfills is required by Federal law. Most states have their own monitoring programs in place at hazardous landfills, and state requirements may often be more rigorous than federal requirements.

Monitoring programs are based on knowledge of the site. Historical records, aerial photographs, and manifests aid in the design of an effective monitoring program.

Monitoring wells are used to detect the migration of hazardous wastes from the interior of the landfill into adjacent ground water supplies. A network of monitoring wells around the perimeter of the site can provide data to aid in the delineation of hazardous waste migration. Monitoring wells and lysimeters can be installed in the landfill interior to serve as an "early-warning" predictor of risk to adjacent ground water resources. Internal monitoring wells are commonly screened either at the bottom of the waste or at the top of the saturated zone (the water table).

Borings performed during well installation can be used to characterize the contents of the landfill. Geophysical logging of the borings can be used to obtain information on the subsurface structure and moisture regime within the landfill. Three types of geophysical techniques are commonly employed for borehole logging (6):

- Natural Gamma Logging - will provide information on clay-rich (daily and intermediate covers) and clay-poor materials (refuse)
- Gamma-Gamma Logging - indication of changes in bulk density; cover material will have greater bulk density than surrounding refuse
- Neutron Logging - indication of moisture content; the probe is also sensitive to hydrogen content of organic materials.

The logging can be performed down the borehole before or after the well casing is installed. If the latter is employed, the density of the steel or the hydrogen content of the PVC pipe must be taken into account. Calibration of the test method should be performed on each site. Due to the instability of the refuse in landfills, open boreholes frequently collapse around the probes, resulting in an unanticipated excavation to retrieve the radioactive source. NRC licensing is required for such logging procedures and calls for the service of a licensed subcontractor.

The distribution of wells on the site is ultimately dependent upon the investigator's confidence in the uniformity of the site. If no information is available as to the contents of the landfill or the leachate chemical characteristics, then at least one leachate well should be installed for every 5 acres of fill area (7).

Several precautions should be taken while installing monitoring wells within the interior of a landfill. O'Hara et al. (8) discuss the seriousness of exploratory sampling and monitoring well installation at landfills containing buried drums. If drums are present on the site, they must be located by non-intrusive, remote interrogation procedures. O'Hara et al. (8) employed a magnetometer to indicate the possible presence of buried metal (including drums). The boring locations were based on the representative distribution within the reportedly deepest portions of the pit and in areas having lower magnetometer readings than surrounding areas. The purpose of the magnetometer screening was to minimize the potential risk of drilling directly into a drum or pocket of drums, particularly at shallower depths. A more detailed discussion of remote interrogation methodologies is presented in a later section of this chapter.

If the investigator has prior knowledge of exactly what radionuclides or chemicals were placed in the landfill, the job of selecting indicator compounds or elements for leachate monitoring is fairly straightforward. Volatile organic compounds are present at most sites, and it has been suggested that they be used as indicators for the presence of other organic compounds (9,10). Thus, without any information on the contaminants that may be present, as a first choice, volatile organic compounds should be monitored as indicators of other organics. For inorganic contaminants, there is no ubiquitous element that can be used as an indicator. The Superfund Public Health Assessment Manual contains procedures for identifying the major contaminants (indicator chemicals) at a site (11).

Soil-Gas Monitoring

Soil may be a small percentage (< 10%) of the bulk material in a landfill. Thus, the term "soil gas" may be a misnomer in the case of landfills, so the term "landfill gas" will be used instead. Landfill-gas analysis can serve a variety of screening purposes, from initial site reconnaissance to remedial monitoring efforts. Obviously, landfill-gas sampling is intended for contaminants with suitably high vapor pressures and, as such, is applicable to the volatile organic class of indicator compounds. Table 5-1 presents the types and concentrations of volatile organic compounds measured in landfill gas at 340 sites in California (12).

Landfill-gas probes can be installed around the perimeter of the site and/or within the site boundary. Samples can be collected in evacuated Summa canisters and the contents analyzed at an off-site laboratory. Field portable instruments are gaining acceptance in the scientific community. They allow immediate on-site analysis of solid, liquid, and gaseous samples. Field analysis of landfill gas is usually by hand-held detectors, portable GC or GC/MS, long-path Fourier transformed infrared (FT-IR) detectors, ion mobility spectrometers, industrial hygiene detector tubes, and, recently, fiber optic sensors. Further information on field screening methods is presented later in this chapter.

Table 5-1. Concentration statistics of specified contaminants and methane in landfill-gas samples.

Compound	Number of Landfills Contaminant Detected[a]	Median[b]	Average	Maximum[b]
methane	258	9.5	19	73
perchloroethene	241	38	1,100	45,000
trichloroethene	228	30	840	11,000
methylene chloride	197	37	4,800	160,000
1,1,1-trichloroethane	180	2u[c]	650	96,000
benzene	180	132u	650	480,000
vinyl chloride	160	106u	2,200	72,000
ethylene dichloride	65	5.1u	600	98,000
chloroform	58	0.8u	360	11,000
carbon tetrachloride	31	1.2u	11	2,100
ethylene dibromide	24	0.3u	4	660

[a] Landfill gas sampling was conducted at 340 landfills.

[b] Medians and maxima of the average sampling results from individual sites.

[c] u = Means non-detected; the number shown is the detection limit.

Note: Concentrations are in ppbv, except methane which is in percent. Taken from Baker et al. (12).

Emission Rates and Characteristics

Vapors emitted from the surface of landfills may pose health risks to adjacent populations. Typically, a flux chamber is used to estimate landfill gas emission rates (13). The Air Resources Board of the State of California recommends that the following compounds be analyzed (12): methane, oxygen, carbon dioxide, nitrogen, vinyl chloride, benzene, ethylene dibromide, methylene chloride, perchloroethene, carbon tetrachloride, 1,1,1-trichloroethane, trichloroethene, and chloroform. The occurrence of these compounds emitted from the surface of landfills is similar to the data shown in Table 5-1 for landfill gas.

The extent of gaseous emissions from the surface of a landfill can often be delineated by observing the distribution of vegetation on the site. Dead vegetation or areas devoid of vegetation can give an indication of areas of gaseous emissions. Gaseous emissions can kill plants by displacement of oxygen from the soil or by direct toxicity.

Long-path FT-IR is useful for the qualitative and quantitative measurement of VOCs and low-boiling semivolatile organic compounds in the ambient air above the surface of hazardous waste sites. Though this technology is sensitive to meteorological conditions such as wind, particulate matter, humidity, and rain, most of these affect point sampling by canister or direct air sampling methods as well.

Geophysical Techniques

Geophysical techniques are frequently applied to characterization of landfill sites. These techniques have been used successfully to delineate contaminant plumes, locate buried drums, map the location and extent of pits and trenches, and assess the general geologic setting of the site. The reader is referred to Telford et al. (14) and Sharma (15) for general works on geophysical techniques. An expert system to assist in selecting the appropriate geophysical techniques for a given study has been developed by EPA (16).

Direct-current and low-frequency alternating-current resistivity determinations usually are made by measuring the voltage drop between two electrodes placed in the ground after an electrical current has been induced in the ground between two other electrodes. The most commonly applied electrode configurations are referred to as the Wenner and Schlumberger arrays. Ultimately, the electrical "soundings" can be related to the presence of a contaminant plume. Dissolved contaminants and buried wastes frequently cause ground water to have an abnormally low resistivity. Great caution should be used when interpreting the results of resistivity measurements. Improper selection of equipment and arrays, poor field procedures, improper interpretation, and irregular terrain all can contribute to difficulties inherent in resistivity determinations. Meaningful resistivity measurements cannot be achieved in landfills where there is a highly random scattering of metallic and other conducting materials present in the heterogeneous matrix (17).

Electromagnetic (EM) surveys are similar to resistivity surveys inasmuch as they also measure electrical properties of the subsurface. EM does not require the implantation of electrodes in the ground, thus making it faster and easier than resistivity. It is also better suited for sites with a preponderance of asphalt or concrete slabs and for sites with highly conductive surface soils. EM is not as susceptible to metallic interferences as resistivity. However, EM is prone to interferences from spurious electromagnetic fields such as power lines, underground cables, and transformers, which are often present at landfill sites.

Magnetometers, such as proton procession devices, are very useful for detecting buried ferromagnetic materials, especially buried drums. A magnetometer can be used to locate drums prior to well installation or removal activities.

Ground-Penetrating Radar (GPR) is capable of detecting, in real time, shallow earth profiles of dielectrical discontinuities related to subsurface conditions such as moisture content, lithology, bedding, voids, fractures, and man-made objects. When conditions are optimal, which seldom is the case on a landfill, GPR profiles exhibit the greatest detail and resolution of any technique. Radar waves are dampened by moist, low-resistivity clays, or other conductive material.

Tracer Studies

Frequently used in hydrogeology, a tracer is matter or energy carried by ground water which will give information concerning the direction of movement and/or velocity of the water and potential contaminants that may be transported by water (18). Tracer studies are not commonly performed on landfills. The physical and chemical behavior of the tracer should be similar to the anticipated contaminant's behavior.

Aerial Photography

Aerial photography and infrared imagery can be powerful tools for defining sources of contaminants on a much broader scale, i.e., the entire landfill site. Aerial reconnaissance to determine the distribution of drums, lagoons, discolored soils, and vegetation over the site can provide useful information about the extent and source of contamination. Subsequent sampling efforts can draw on this source of information to focus on hotspots and problem areas.

Waste Sampling

As discussed earlier, intrusive sampling of landfills is costly, labor intensive, and dangerous. It is usually only performed when the final disposition of the site has been determined to be waste removal or treatment.

Chapter 3 describes how data needs are defined and a sampling strategy is developed. No standardized approach is available for sample acquisition at landfill sites. Each landfill waste characterization project is unique. Questions to be asked when collecting samples from a landfill for hazard characterization include:

- What part of the landfill should be sampled?
- Which items should be included as part of the sample?
- Should samples of heterogeneous materials be composited? If so, how?
- How much of each type of material should be collected?

Sampling Location

The location from which to collect samples at a landfill site is determined from information acquired by the application of many of the same nonintrusive techniques discussed previously: photographs, historical records, manifests, and conversations with people familiar with site operations.

As much as possible should be learned about the site prior to sample collection. Review of aerial photographs, historical records, and manifests can provide a great deal of information as to the nature and location of wastes on the site. Conversations with waste haulers who delivered wastes to the site can provide insights not available from historical records or manifests.

A walk-over inspection of the site should be performed to gather information on a smaller scale. This approach is semiquantitative. Quadrants are laid out over the landfill, and field personnel sketch or photograph debris on the surface of the site as they walk over each quadrant. Debris is not handled or disturbed during the walk-over survey. Photographs and sketches can be later inspected off-site, thus greatly reducing the amount of time field crews are on the site. Subsequent sampling operations can focus on areas with possible sources of hazardous materials using evidence gathered during the walk-over.

If the landfill is inactive or abandoned, both historical and newly-acquired aerial photographs are invaluable in inventorying and evaluating the site. Historical aerial photographs are particularly useful in inactive waste site investigations. They are not only useful in compiling land use/cover, environmental, and other physical site-specific data, but also in directing ground investigation teams to exact locations for conducting drilling and leachate sampling operations.

Various state and federal agencies have photographed most of the United States in recent years. As discussed by Erb et al. (19), at least one photograph exists for any land area within the continental United States. Most of the federal photographic data has been catalogued by the U.S. Geological Survey's National Cartographic Information Center (507 National Center, 12201 Sunrise Valley Drive, Reston, VA 22092, 703-860-6045).

Screening Techniques

Ground Penetrating Radar (GPR) and Magnetometers--On many landfills, particularly those located on industrial plant sites, drums are the most common solid waste. Concerns about public and occupational health and safety may make investigators hesitant to directly drill or dig into buried drum disposal sites. As described earlier, GPR and magnetometry are two nonintrusive methods that can be used to locate pockets of drums or individual drums prior to sampling.

Landfill Gas and Emission Gas--Landfill-gas and gaseous-emission surveys can be used to focus sampling efforts. Elevated levels of VOCs in samples collected from landfill-gas probes or flux chambers can be indicative of subsurface zones contaminated with VOCs. Sampling for isolation and remediation of these contaminated zones can be guided by the data collected during these surveys (12).

Sample Collection

Excavation--Once the area to be sampled has been identified by nonintrusive methods, a set of actual representative samples of the debris present in the landfill is collected. Common sense and experience are key ingredients in effectively and safely obtaining samples from landfills and waste piles. The hydrogeologic setting will also influence sampling device selection.

Various excavation procedures are used to bring subsurface refuse to the surface for sampling. Test pits give a more representative cross-sectional view of the landfill structure than can be obtained from discrete samples or cuttings from borings. The wider cross section exposed and the greater amount of material available for sampling can give the site investigator greater confidence that the samples collected and analyzed are representative of the overall composition of the subsurface material. Transect trenches can be dug to systematically sample the site. Hill and Montgomery (7) have developed an approach for installing test pits at hazardous waste landfill sites. Prior to test pit excavation, the cover material is removed and segregated by a bulldozer. This material can later be used as a cap after the pit is backfilled. Test pits are generally excavated with a backhoe, which limits the depth of investigation to approximately 20 feet. The authors have used backhoes equipped with custom-built arms or draglines for excavating below 20 feet, but find that hourly equipment costs increase substantially with depth. Hill and Montgomery (7) have found that placing excavated wastes on plastic sheets to prevent migration of contaminants is awkward and ineffective, so in their work the waste material is placed on stripped areas to avoid inadvertent contamination of the surface material. Backhoes dump the waste out and the material is physically characterized by field workers. The material is photographed at all phases of the operation. The types of materials and their frequency distribution within each load is determined. The amount of water (liquid) is determined. Elaborate and complete documentation by the sampling personnel is essential.

Ideally, the location of drums on the site has been predetermined by GPR, magnetrometry, or other appropriate remote interrogation procedures. However, unexpected encounters with randomly scattered drums will inevitably occur. The backhoe operator should be experienced with drum detection and retrieval. Overpacks for containing ruptured drums and a small pump and/or adsorbent for recovering releases should be immediately available. Large-scale drum removal and containment is best handled by qualified removal contractors as an emergency removal or as part of site remediation activities. For further guidance on drum excavation and removal, the reader is referred to a separate document on drum-handling practices at hazardous waste sites (1).

Drilling--When refuse depths exceed 20 feet, drilling is another technique for acquiring subsurface refuse samples. Horizontal drilling has also been used to obtain material from the interior of waste piles. Drilling can be safely performed on drum disposal sites by the proper utilization and interpretation of GPR or magnetic methods (8). Typically, a truck-mounted rotary drill rig similar to those used for ground-water monitoring well installation is used for refuse drilling. Air rotary equipment should be avoided, especially when VOCs are present, because it increases the release of airborne contaminants. Hollow-flight augers are the most effective for refuse sampling in landfills. A continuous cased core is collected which allows for identification of perched liquids. When hollow-stem augers are used, the cores can be field-screened by XRF or hand-held organic vapor detectors for the presence of heavy metals or VOCs, respectively.

Water does not necessarily have to be introduced into the borehole unless there is a concern over the release of potentially harmful contaminants into the ambient air. In such an instance, clean water can be introduced to prevent venting of hazardous landfill gases (it should be borne in mind that this can cause cross-contamination between cells of the landfill).

Hill and Montgomery (7) estimate that up to 25% of drilling footage in landfills will be terminated due to encounters with impenetrable zones, such as automobiles, refrigerators, transformers, and the like. Appropriate adjustments in the projected cost of drilling should be made.

Rathje (20,21) collects samples from municipal landfills for anthropological studies using hollow-stem augers. The contents are unloaded onto sheets of plywood for characterization. The items on the plywood are placed into plastic bags for later sorting off-site. This may be acceptable for municipal landfills that supposedly contain no hazardous constituents. However, Baker et al. (12) have found no significant difference in the amount of hazardous VOCs present in landfill gases from hazardous and reportedly nonhazardous landfills.

Manual coring devices can sometimes be used to collect subsurface samples on landfills or within waste piles. These devices, commonly used for soil sampling, include split-spoon samplers, Shelby tubes, and zero contamination samplers. Dry solids are best sampled with a concentric tube thief. These various devices are much smaller in diameter than hollow-stem augers and will accordingly obtain smaller samples. The smaller sample size may not accurately represent the diverse material present in the landfill. Only materials that fit inside the sampler will be retrieved. However, these devices may be suitable for sampling the landfill cover material, which usually consists of a fairly homogeneous layer of soil. For obtaining estimates of VOCs present in the near surface materials, intact subsamples may be removed from the coring devices with small-diameter hand-held coring devices. The contents of the hand-held corer are extruded directly into 40-mL glass volatile organic analysis (VOA) vials for subsequent purge-and-trap analysis (22). Several samples can be composited in a jar containing purge-and-trap grade methanol to obtain a more spatially representative estimate of VOC concentrations in the near surface matrix. Alternatively, samples from the split-spoon sampler can be sectioned and placed in wide mouth jars containing methanol (22,23). The methanol serves to preserve the sample by reducing losses of VOCs by volatilization (it should be noted that this is not currently a standard procedure; it is a draft ASTM procedure introduced as an alternative to Method 8240).

Crude Sampling--Finally, near-surface material can be exposed using crude sampling implements such as shovels, picks, and trowels. These procedures are suitable for metals and semivolatile compounds, but will cause losses of VOCs due to excessive disturbance.

Sample Handling

Sieving--Investigators sampling debris at landfills frequently separate materials by size, although it should be borne in mind during project planning that the contaminants are not likely to be uniformly distributed among the size fractions. The material exhumed by a backhoe, auger, corer, or crude sampling device can be passed through a sieve. For estimation of bulk components, the smaller size fraction may be excluded from the sample. Wilson and Rathje (21), in characterizing municipal landfills for anthropological studies, passed the material obtained using a backhoe through a ½-inch mesh. The material passing through the screen was discarded while the retained portion was sorted and identified. Usually at hazardous waste landfills, information about contamination associated with a range of size classes is needed for remedial planning. The smaller items are more easily handled by the laboratory, are more amenable to a variety of remedial techniques, and, due to their greater surface-to-volume ratios, can potentially leach more contaminants into the landfill. Thus, the finer material that passes through the mesh can be subsampled with a corer or scooped into bags or sample containers for analysis. The retained fraction can then be placed in a sample container for subsequent leaching or extraction procedures. Items too large to fit into a container can be wipe tested. In a removal program, sieving is generally only conducted when preparing soil samples for x-ray fluorescence (XRF) field screening. A 20-mesh screen size is recommended for this purpose. Samples taken for VOA should not be sieved.

Determining which items to exclude from the sample is a difficult issue to address. Not all items contribute to the hazard posed by the landfill site. Inclusion of all items may introduce error in the sampling and analytical procedures. Examples of extraneous material may include twigs, leaves, or pieces of glass. In a very *ad hoc* manner, some investigators exclude all items larger than 3 inches, i.e., "too big to fit in the jar," from the sample. Objects larger than ⅜ inches were excluded from samples to be used for a bench-scale stabilization treatability study (24). However, some large items are essential contributors to the hazardous nature of a sample or site. For example, battery casings may release considerable amounts of lead and should therefore be included as part of the sample. Laboratory constraints must be known before the project planners specify collecting samples containing large items for analysis.

Comminution and Homogenization--Some investigators have obtained homogeneous samples from a mixed matrix of refuse by comminution and homogenization of the material. Commercially available shredders can be used for this purpose. The American Society for Testing and Methods (ASTM) has standard procedures for determining the efficiency of refuse size-reduction equipment (25). However, no guidance is offered for exactly what items may be fed through such equipment. Obviously, not all items are amenable to comminution, either because of their size, particular analytical concerns, or safety considerations. The drawbacks to comminuting heterogeneous wastes are enumerated below, under "Comminution of drum contents." If comminution will be performed on the site, waste incompatibility should be determined first. Hatayama et al. (26) have provided guidance on waste incompatibilities that can be useful during waste comminution processes. These authors have developed a "Hazardous Waste Compatibility Chart" that allows the user to evaluate potential adverse reactions for binary combinations of hazardous wastes. Binary waste combinations are evaluated in terms of the following reactions: heat generation from a chemical reaction, fire, toxic gas generation, flammable gas generation, explosion, violent polymerization, and solubilization of toxic substances.

Sorting and Segregation--After refuse has been passed through a sieve, the retained items may be further separated by sorting or segregating by material type, size, or hazard class. Sieving may not necessarily precede sorting. There may be a preponderance of large items that would make sieving impractical.

The ultimate disposal or remediation approaches under consideration dictate how debris is sorted (see discussion on establishing waste populations, Chapter 3). The treatability of the waste should be determined early in the process and should be considered when sorting heterogeneous materials. Samples may be sorted to obtain representative material to determine the efficiency of incineration, for example. Treatment or disposal options for specific waste types are covered in detail in numerous reports. The EPA (27) prepared a useful summary of major treatment and disposal options for various waste categories.

The presence of hazardous substances in the sorted debris can be tested on site using numerous field screening methods (28). These include XRF analysis for heavy metals, vapor monitoring or field GC analysis for VOCs, and high-vapor-pressure semivolatiles. Field test kits are available for screening-level analysis of PCBs. However, the EPA requires that samples of record be laboratory tested for PCBs before they are combined or composited. Testing to determine gross halogen content can sometimes be foregone if all insoluble wastes are to be incinerated at a facility capable of handling chlorinated organics. However, testing for PCBs is required, regardless of the need for testing other halogenated compounds.

Containerized liquids within the sorted material can be tested for compatibility by mixing small samples and making visual observations for precipitation, temperature changes, or phase separations. After compatibility has been determined, if the debris is uncontained, it is often put into drums for removal and subsequent disposal or treatment. The drums should be inventoried and labelled as they are filled in order to avoid resorting the drums at the disposal or treatment facility.

Large-scale Extraction--On-site batch extractions of bulky, heterogeneous wastes may give the most reasonable representations of the hazards posed by these materials. Such tests are not often performed. They are most appropriate when contaminant leaching from the surfaces of large objects is the major concern. Sorted and unsorted waste is weighed and placed in a 55-gallon drum. Water or another leaching fluid is added to the drum and the drum is placed on a drum roller. A batch leaching test of fixed duration is performed on the material in the drum. The leachate is then collected and aliquots are analyzed for the compounds of interest. The remaining fluid may have to be drummed and treated as hazardous waste. Such tests are not standard, and their use must be negotiated with the regulatory agency during project planning.

Wipe Tests--The hazardous chemicals associated with the exterior surfaces of large items are also commonly characterized by wipe tests. In these tests, a unit surface area (usually 0.1 or 0.5 m^2) is wiped with a dry or solvent-moistened swab, and the swab is then extracted and analyzed. Wipe test results give no information on total contaminant level and are difficult to interpret with respect to health or environmental risk. Wipe tests are frequently used on concrete surfaces. However, concrete is fairly porous, and contaminants from the interior of the material can migrate outward after the wipe test has been performed. Some investigators no longer use wipe tests but rather disaggregate the concrete into small chunks with a jackhammer, and then perform a TCLP extraction on ground-up chunks of concrete. Leaching tests of large items the size of transformers are being developed by the EPA. The efficacy of the washing (leaching) procedure is evaluated by before-and-after wipe tests of surfaces on the debris (29). One of the problems with wipe tests at present is that there are no rules of thumb for appropriate action limits in terms of concentration per unit surface area.

Containerizing--If representative samples cannot be effectively screened in the field, then subsamples must be returned to the laboratory for analysis. A wide assortment of containers are commercially available for sample collection. The type of container selected is dependent upon the size of the item(s) and the type of contaminants to be analyzed. Wide-mouth glass jars, typically 125-mL or 250-mL, are used for organic analytes. Immersion of solid samples into wide-mouth jars containing methanol has been shown to reduce losses of VOCs (22). Five-gallon ORME pails are commonly used to obtain treatability samples.

Sample Shipping--Samples collected in the field may be composed of hazardous material or have a component that is hazardous. The samples are often transported to off-site laboratories for analysis. Therefore, there should always be a person in the field who has experience with DOT regulations for shipping of hazardous materials (30). Samples immersed in methanol are required to be shipped as a "Flammable Liquid." Documents accompanying the shipment must alert the laboratory to the anticipated hazard level of the samples.

Field Screening Methods

Existing Methods

Many field screening procedures are useful for determining the presence of various contaminants in landfills, waste piles, or drums. A review of all available procedures is beyond the scope of this document, but a brief description of a few procedures follows. For more information, the proceedings from the first and second international symposiums on "Field Screening Methods for Hazardous Wastes and Toxic Chemicals" (31,32) as well as the "Field Screening Methods Catalog: User's Guide" (28) should be consulted. A new version of the latter document is in preparation and will be called the "Field Analytical Methods Catalog" (33). As planned, the document addresses analyses for volatile organics in water, soil and sediment, soil-gas, and air; semivolatile organics; pesticides; polychlorinated biphenyls; polynuclear aromatic hydrocarbons; inorganics; and classical analyses.

X-Ray Fluorescence--Toxic metals can be screened using a field portable XRF unit. The XRF has a limited depth of penetration, i.e., a few millimeters. The depth of penetration is dependent upon the matrix. Various components of a waste pile may be scanned to determine toxic elemental concentrations on the exterior of the pile. XRF screening can be used in conjunction with sorting to isolate components of a waste pile that exhibit elevated levels of a particular toxic metal.

Organic Vapor Analyzers/Gas Chromatographs--Organic vapor analyzers (OVAs) have been used for many years in the industrial workplace. OVAs are usually equipped with a photoionization detector (PID). Organic chemicals whose volatility is sufficient to allow their partitioning into the ambient air can be detected. The PID is somewhat limited as to the types of compounds it can detect. Most aromatic hydrocarbons (e.g., benzene, ethyl benzene, toluene, and xylene) are detectable using a PID. However, only certain halogenated VOCs, such as trichloroethene and perchloroethene, can be measured. Only total hydrocarbon concentrations are measured using the OVA. No information is obtained regarding the exact identity of compounds present. The level of organic contaminants that can be detected varies with environmental conditions such as wind speed and direction, humidity, rainfall, and temperature. OVAs can also be used to scan liquid and solid samples obtained from the interior of the pile by intrusive sampling methods.

Field portable gas chromatographs (GCs) are gaining recognition as a viable means of identifying and quantifying VOCs and some semivolatile organic compounds. A range of detectors are available, allowing detection of a broad assortment of VOCs and semivolatiles. Liquid and solid samples can be screened by headspace analysis (28). More recently, field portable GCs equipped with mass spectrometers are being used on hazardous waste sites for confirmational analysis (34).

Ion Mobility Spectrometers--The ion mobility spectrometer has been used in the past for detection of narcotics and explosives. Recently, it has demonstrated its usefulness for screening of hazardous waste sites for volatile compounds. It is capable of detecting many different classes of compounds, ranging from amines to acids. It can be used as a class detector (e.g., esters, ketones) or to identify specific chemicals. The high sampling flow rate, usually measured at several liters per minute, makes it ideal for "sniffing" around piles and dumps for the presence of a diversity of hazardous materials.

Cone Penetrometer--Cone penetrometers were originally designed to assess soil strength properties for railroad grades and unpaved roadways. Soil strength is determined by measuring the resistance developed on the cone tip and on a fixed area (sleeve) of the rod behind the tip. The tip resistance and sleeve friction vary with grain size of the soil and the degree of compaction or cementation. Penetrometers are becoming increasingly popular as hazardous waste sampling devices because they combine speed and versatility with a degree of safety that is not available in conventional drill-and-sample operations. Sensors are now available for measurement of electrical conductivity of soil, natural radioactivity, and soil optical properties (fluorescence and reflectance). The penetrometer, coupled with the appropriate sensors, has been used to locate and track fluorescent tracer dyes and waste oil and fuel in natural soils and landfills (35). The penetrometer can provide information regarding the density of the interior of the pile and the presence of hazardous chemicals.

Open-path FT-IR--Open-path FT-IR is useful for the qualitative and quantitative measurement of VOCs and low-boiling semivolatile organic compounds in the ambient air surrounding the surface of hazardous waste piles. Though this technology is sensitive to meteorological conditions such as wind, particulate matter, humidity, and rain, most of these also affect point sampling by canister methods as well.

New or Developing Technologies

Fiber-Optic Chemical Sensors (FOCS)--These allow *in situ* monitoring of ground waters. This developing technology is based on chemically selective optical fiber transducers. The chemically modified optical sensors can be configured for either single or multiple component characterization (36,37). Optrodes can provide rapid, sensitive measurement of temperature, pH, anions, cations, and organic pollutants. Sensors for pH, Ca(II), Pb(II), Se(IV), As(III), Hg(II), CN^-, O_2, CO_2, $CHCl_3$, CCl_4, C_6H_6, perchloroethene, trichloroethene, and benzo(a)pyrene have been or are being developed. Miniature, fully integrated remote-sensing modules that incorporate chemically selective, microporous membranes on optical fiber bundles with laser excitation sources, fluorescence detection, and a microprocessor transmitter/receiver for telemetric surveillance are being developed. These systems will provide accurate sampling with lower analysis costs and greatly reduced sample handling requirements. FOC sensors have the same drawback as many other sampling/sensing techniques: they yield point measurements, which must be appropriately integrated to achieve representativeness.

Raman Spectrometry--Surface enhanced Raman scattering (SERS) has shown improved selectivity and sensitivity for detection and screening of trace level contaminants in ground water. The narrower Raman bands simplify identification of individual components in complex mixtures. The feasibility of utilizing SERS in harsh environments has been demonstrated, and new substrate and optrode designs are being developed.

Laser Ablation (LA)-Inductively Coupled Plasma (ICP) Atomic Spectrometry--The technique involves the generation of aerosols from solids and the introduction of these aerosols into a high temperature (~6,000-10,000K) argon inductively coupled plasma. At the high temperatures, the sample is dissociated and atomized. The free atoms undergo excitation and ionization to provide characteristic optical and mass spectra of the constituent atoms and/or ions. ICP-Atomic Emission Spectrometry (AES) is currently the most widely used analytical technique for the detection of more than 70 elements. LA-ICP-AES provides a means of analyzing solids directly by sweeping the ablated particles into the ICP. The advantage of laser ablation sampling is that it eliminates or minimizes the need for routine sampling, labelling, transportation, sample preparation, analysis, and disposal of the sampled material. It is also applicable to nonconductors as well as conductive materials. LA-ICP-AES is currently being developed as a method for remote field applications. Small volumes of liquids can also be efficiently sampled using a direct injection nebulizer, and then analyzed using remote ICP-AES. ICP-mass spectrometry (MS) provides detection capabilities approximately three orders of magnitude better than ICP-AES. Mass analysis provides necessary elemental isotopic determinations. ICP-MS instruments, which use laser ablation for sample introduction, are commercially available, and field portable mass spectrometers are being developed. ICP-Laser Excited Atomic Fluorescence Spectrometry (LEAFS) can provide additional selectivity that minimizes or eliminates spectral interferences for direct isotopic analyses in complex sample matrices. Advances in diode lasers will make LA-ICP-LEAFS an attractive isotope specific field technique.

Laser Induced Breakdown Spectroscopy (LIBS)--Focusing a high intensity laser pulse in liquid, gas, or solid samples can produce a spark. The spark is a result of dielectric breakdown of the medium induced by the strong electric fields of the pulse. The high temperature spark plasma reduces the material to elemental form and also excites the species. Emitting ions, atoms, and simple molecules are identified by their characteristic spectral lines. LIBS has been used to detect atoms in vapors, aerosols, and particles. LIBS has also been used to determine uranium in solution for possible application to process control in nuclear fuel reprocessing facilities. Real-time analysis is possible because the laser spark both vaporizes and excites the sample. The technique is also non-intrusive in the sense that only optical access to and from the sampled medium is required.

Laser Induced Fluorescence (LIF)--This technique uses relatively low power laser excitation transmitted through fiber optic cables to samples, and the collection of the resulting fluorescence emitted by the species, again through fiber optics, for selective spectrochemical analysis. The selectivity of the technique is enhanced by the capability of generating excitation and emission spectra, as well as by utilizing time resolution. The technique is currently targeted at the determination of polycyclic aromatic hydrocarbons (PAHs) in ground water, gases, and soils. A rugged, field transportable tunable dye laser system has been tested. LIF has been tested for PAH determinations using cone penetrometer technology.

Characterization of Contained Heterogeneous Wastes

In characterizing contained wastes, the preferred approach is to minimize intrusion into the waste and minimize waste handling, to curtail risks to personnel. For materials contaminated with transuranic wastes, the preferred hierarchy of waste characterization approaches is to identify container contents and contaminants from records and knowledge of the original waste stream; then perform non-intrusive interrogation; next make a minimal intrusion for headspace sampling; and finally, if absolutely essential, perform intrusive sampling. An alternate approach that is always available is to minimize the waste characterization needs by specifying a very robust waste treatment process that could handle all possible materials and contaminants. This would eliminate the costs and risks of a full characterization study. If intrusive sampling is required, it may be possible to sort containers based on non-intrusive or minimally intrusive techniques and more fully characterize each population. The statistical aspects of this approach are discussed in Chapter 3.

Non-Intrusive Techniques

Real Time Radiography

Real time radiography permits an operator to remotely observe the contents of a container using x-rays. Excellent resolution is obtained and it is possible to detect free and contained liquids, metals, individual objects, granular material, aerosol cans, gas cylinders, wood, etc. The resolution is often good enough to determine whether an aerosol can has been punctured and to detect a few milliliters of liquid in a 55-gallon drum. The devices are commercially available and are estimated to cost $1.5-1.7 M for a box (4x4x8 ft) size unit including training and installation. With digital image processing/x-ray tomography, the device is better able to distinguish between metals depending on their density. However, at high densities, differentiation becomes more difficult and time consuming.

Sonar scans are frequently used to determine drum integrity as part of real time radiography.

Radiation Measurement Instrumentation

Measurements of gamma rays and neutron emissions enable non-intrusive determinations of nuclear materials contained in drums. Radiation instrumentation is based on detection of alpha and beta particles, gamma rays, and neutron emissions. Alpha and beta particles will not penetrate the wall of a drum and therefore have limited application in screening the contents within a drum. Measurements of gamma and neutron radiation allow quick screening of the interior contents of a drum. Gamma and neutron measuring systems are classified as passive or active. Passive measurements depend on measurement of intrinsic radiation emitted by decay and interaction of materials within a sample such as gamma emission following decay, spontaneous fission neutron emission, and (alpha, neutron) reactions. Active measurements induce a reaction in the sample that produces measurable radiation such as using an x-ray generator to measure the edge of a material, and neutron source to produce fissions in nuclear material or as elemental analysis through neutron activation analysis.

Gamma-Ray Assay Methods--Gamma-ray assays rely on either low-resolution detectors such as NaI that are unable to resolve individual gamma-ray peaks or high-resolution detectors such as intrinsic germanium that allow sufficient resolution to identify specific radionuclides. Since gamma rays are directional and easy to collimate and filter, they can be used to determine the precise location and distribution of radionuclides (38). Segmented gamma-ray scanners involve the use of collimated detectors to examine multiple segments or pancake-shaped sections of a drum. They can be used for screening or for quantitative detection and location of nuclear materials such as ^{235}U and ^{239}Pu in containers up to 55 gal.

Neutron Assay Methods--Neutron techniques generally measure large samples, in comparison to gamma-ray methods, and have the advantage of good penetration and application to a wide variety of samples (38). Both passive and active techniques exist and may use the same detectors. Several neutron emission screening devices exist including:

- Portable hand-held total neutron monitors which can be used to detect neutrons from spontaneous fissions (i.e., plutonium, californium, curium and other gamma and neutron emitters)

- Passive neutron coincidence counters which measure containers ranging in size up to 55 gal. drums to determine the presence of spontaneous fissions from nuclear materials such as plutonium

- Active well coincidence counters that use a random neutron source (i.e., Am, Li) to produce a fission in nuclear materials such as uranium for measurement by coincidence counting

- Combined passive and active coincidence counters which allow measurement of uranium and plutonium plus transuranic elements

- Active neutron interrogation which uses an external source such as ^{252}Cf for sample irradiation and delayed neutron counting or a deuterium-tritium (DT) neutron generator for differential die-away assay of nuclear materials and transuranics in a drum. These systems have sensitivities below 100 nCi/g of transuranics

- Passive coincidence counting and active measurements can be combined to enable one system to provide both passive and active assay, such as the active well coincidence counter, Shuffler, or DT system

- Neutron activation analysis (NAA) is a non-invasive elemental analysis technique potentially suitable for materials contained in drums, including non-radioactive materials. It uses high resolution gamma-ray measurements with active neutron systems such as the Shuffler and Differential Die-away systems. Additional development is required to determine the overall capabilities for elemental detection and to determine what sensitivities are achievable. The prompt gamma neutron activation probe is very sensitive to chlorine, and may provide a non-intrusive technique to assay for chlorinated solvent vapors in the headspace of drums. Chapter 6 describes the potential applicability of NAA techniques in more detail.

Quantitative and semi-quantitative assays using radiation-based techniques are dependent on appropriate calibration, development of reference standards, and a measurement control program that includes operator training.

Limitations

Metal salts, powdered metals, the identity of liquids, and the presence of vapors within waste containers cannot be detected remotely at this time.

Minimally Intrusive Techniques

Headspace analysis is a minimally intrusive technique that can be used to determine the presence of volatile compounds and explosive conditions. Drums may have to be opened remotely or using non-sparking tools (1) if combustible mixtures may be present. The gas may then be analyzed using a field portable explosimeter, organic vapor analyzer, vapor detection tubes, radiation detection device, or gas chromatograph. Alternatively, headspace gas samples may be collected for off-site analysis using canisters, gas bags, or sorbent traps.

For drums containing radioactive materials, self-sealing sampling ports are available to minimize the potential loss of contents. While radioactive mixed waste may be double and triple bagged, it is expected that diffusion will occur through almost any container so that the presence of volatile and some semivolatile compounds could be determined. In some cases, it may be possible to overpack a drum and, after some time, sample the headspace of the overpack to detect volatiles being emitted from the drum of interest. Research on the feasibility of such an approach is recommended.

Intrusive Container Sampling

Sort Drum Contents

One method of handling containerized heterogeneous waste begins with sorting the contents by material type. In other words, if the container holds clothing, rags, wood, plastic, metal, and paper, the contents are removed and placed in various piles: clothing, rags, and paper in one pile, wood in a second pile, plastic in a third pile, and metal in a fourth pile. The next container is then opened and the procedure repeated, adding to the piles of material from the first container. The process is repeated until all containers have been emptied and all the contents sorted.

After sorting is complete, each pile of material is weighed and sampled. Wood can be sampled by sawing off small pieces from each item. Nonporous material can be rinsed with water or solvent to extract surface contaminants. Materials that have only surface contamination can be wipe sampled. Soft material can be sampled in one of several ways:

- Cut out pieces from each article using scissors or shears until enough material is obtained for a sample.
- Punch holes in the material using something similar to a large diameter paper punch.
- Place the material back into one of the containers. Obtain a core sample using a hand-held coring device.

The samples taken from each material type are then analyzed for the contaminants of concern.

An advantage of this approach is that populations are established and contaminant levels are determined for each material type, not just drum by drum. A major disadvantage is the difficulty of collecting "representative" samples, if that is a goal of the project. Within each material type there is likely to be a wide range of contamination among individual items. Three possible ways to deal with this variation are:

- collect the entire pile of material, or a large portion of it, as the sample;
- collect a number of equivalent samples from the pile to allow a statistical estimation of the range and mean of contaminant concentrations among items;
- deliberately sample the most contaminated objects, if they are evident visually or by field screening. This biased approach will yield an estimate of the maximum contamination level for each material type.

Which of these (very different) approaches is appropriate is decided during project planning (see Chapter 3).

Sort Drums Using Process Knowledge

Another method of handling containers before sampling is to sort them by hazardous constituent based on knowledge of the process that generated the wastes. An example of this approach is the system used at DOE's Fernald Environmental Management Project (FEMP) in Ohio. There, all drums are labeled with a Lot Marking System Number (Lot No.). This number is a 15-digit alphanumeric code that consists of five parts. One of the parts (Material Type) describes the material contained in the drum. Another part (Source Code) identifies the equipment and process that produced the material. Together these codes are used to identify "waste streams." A waste stream is contained in a group of drums that are labeled with the same Material Type and Source Code. For characterization purposes, a waste stream constitutes a single population of interest. All of the materials in one waste stream are either RCRA hazardous for the same constituent(s) or non-hazardous. Also, all of the materials in a waste stream are either high-level radioactive waste, low-level waste, or not radioactively contaminated.

A waste stream that is identified using process knowledge and the container markings may be split into several waste streams when more information becomes available. For instance, analytical data may indicate that a waste stream actually has more than one material. One may be RCRA-hazardous for lead and another may be non-hazardous. If new information indicates that a waste stream actually consists of several different waste streams, then the newly identified waste streams (populations) must be handled separately.

Each waste stream is statistically sampled to reduce the total amount of sampling and analysis required to identify the hazardous constituents (39). At the FEMP, the approach taken is biased toward sampling maximally-contaminated items, since the goal is to identify the contaminants present and ascertain whether any of the drummed objects could be RCRA-hazardous. Field personnel seek out items with stains or surface residues. The list below includes common materials in a heterogeneous waste stream and sampling methods commonly used for these materials at the FEMP.

- Clothing, paper, rags, plastic bags, plastic sheets - These materials are sampled using shears or scissors. Sections of the matrix that appear to be contaminated or stained are cut or torn off in small pieces and placed in the sample container.

- Wood - If the wood is in chip form, sampling personnel remove the necessary quantity to perform the required analyses. If the wood is in large pieces - boards or construction timbers, for example - they locate an area of visible contamination and sample that section. They remove the sample using a saw, hand drill, or auger, and reduce the particle size as required.
- Metal - If there are residues of any kind (sludge, dirt, liquid), they are collected by scraping or wiping.
- Free liquid - If there is any free liquid in the container, it is sampled.

The approach taken is the most conservative, i.e., it targets the most-contaminated items. If for any reason the drum must be resampled, the second sample will probably contain less of the hazardous constituent than the first sample and will be a less accurate estimate of the maximum contamination present.

Comminution of Drum Contents

Comminution of drum contents is a method of reducing the heterogeneous nature of the material before sampling. First the investigator must ensure that the process will not result in explosion, fire, release of toxic gases, or other hazards. Then the contents of the drum are mixed and/or shredded to produce a more homogeneous mass with smaller particle size. Finally, core or grab samples are collected for chemical analysis.

This process is not recommended for the following reasons:

- Chemical compatibility of the drum contents may be difficult to establish. If the materials involved are incompatible, the process could produce explosion, fire, toxic gases, or other hazards.
- Compressed gas cylinders, explosive materials (picric acid, etc.), ignitable materials (solvents, metals, etc.) present hazards if not handled with care.
- Release of dust and contaminants during the process is of concern from a health and safety perspective.
- The process can result in a larger volume of contaminated material by the mixing of previously contaminated and uncontaminated material and the contamination of previously-clean waste containers.
- The mixed matrix may pose greater sample preparation problems than the original waste-digestion problems, increased surface area, etc.
- If volatile organic compounds are present, some will be lost during the process and the corresponding analytical results will, therefore, be unrepresentative.
- Large volumes of material may still be required to provide representative samples, and the material will not be of uniform particle size vis-á-vis laboratory sample preparation procedures.

Treatment After Minimal Evaluation

An alternative to intrusive sampling of heterogeneous material is to assume that the material is hazardous and treat it in a plasma arc furnace. This furnace contains large crucibles that are heated by plasma jets. The crucibles are large enough to accommodate entire drums. Therefore, the drums do not have to be opened. This reduces exposure of personnel to hazardous materials.

Drums of waste are fed into the crucible where they are melted and mixed by the plasma jets. This homogenizes the waste as well as treating it so that it will no longer be hazardous. The temperature is high enough to destroy organic contaminants. If there is enough silica present, the resulting material is a very stable glassy slag. Silica can be added to the melt if there is not enough in the waste. Once the glass is solidified, any hazardous metals in the material are no longer leachable.

The melt can be sampled before or after it solidifies. It can be solidified in several forms, including pieces small enough for the TCLP analysis. Since the material is now homogeneous, the problem of sampling and analyzing heterogeneous material no longer exists.

There are two limitations to this process. First, drums that are full of liquid cannot be put into the furnace because of the potential for steam explosions. This can be prevented through screening the drums by process knowledge or non-intrusive techniques. Drums that are full of liquid can be treated by feeding the liquid in slowly instead of 55 gallons all at once.

The second limitation is that there are currently only two plasma arc furnaces in operation that can handle hazardous, non-radioactive waste, and only one that can handle hazardous, radioactive waste. Consequently, there is a limited capacity for this process. In addition, state governments require that wastes crossing their borders be fully characterized. This defeats the purpose of using this method and leaves the problem of characterizing heterogeneous waste.

Recommendations

1. Additional plasma arc furnaces are needed. In addition, state agencies should be approached with information on the efficacy of the plasma arc furnace technology. Work needs to be done to change the restrictions on the shipment of waste to these facilities and to develop portable units.

2. Research is needed to develop techniques to identify metals and organic compounds remotely, without opening containers. In particular, a testing program should be conducted to assay the ability of prompt gamma-ray analysis to detect chlorinated organic compounds in drums non-intrusively.

3. Further development and commercialization of new field analytical and screening techniques is recommended. These techniques have the potential to greatly diminish the need for sample handling and, to some extent, to circumvent the question, "What should constitute a sample?" that is so difficult with heterogeneous materials.

4. Clear guidance is needed for appropriate chemical parameters to be monitored at hazardous waste landfills. There is currently a considerable waste of resources in analyzing for the entire priority pollutant list. Enough information exists to select appropriate indicator compounds for landfill sampling and monitoring.

5. Tracing contaminant migration at landfills by standard soil-gas monitoring techniques is not an accurate technique, because the partitioning of VOCs between the sorbed and gas phases is different in debris than in soil. Bench-scale experiments are recommended for common types of wastes, to define the partitioning parameters, and provide guidance on the appropriate use of soil-gas monitoring at landfills.

6. The development of one or more standard, large-scale field extraction tests is recommended. The appropriate leaching solvent for these tests may be site surface or ground water.

7. In specialized coring applications, the construction industry is now using very large hollow-stem augers that create boreholes up to 8 feet in diameter. Large objects can be recovered from within the borehole using tongs. While they are quite costly to mobilize/demobilize, these "super augers" might have utility in some landfill studies and should be investigated for this use.

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Chapter 6

Analytical Laboratory Requirements

Clare Gerlach, Wayne McMahon, and James Poppiti

Introduction

The topic of the chemical analysis of heterogeneous wastes can be subdivided variously to address any of several situations arising from the sampling of a complex debris site. If the heterogeneity is dealt with by the field samplers (i.e., physical segregation is done on site), the samples received by the analytical laboratory may be homogeneous though they are substituents of a vastly heterogeneous population. Alternatively, physically diverse materials may be packaged together and submitted as a unit to the laboratory. The responsibility then falls on laboratory personnel to decide whether to analyze the whole sample or to separate or homogenize it before performing the analysis. Thus there are three basic options for the laboratory in dealing with heterogeneous waste samples.

Within these options additional levels of complexity are possible. Sometimes a multiphase liquid sample is received, and obtaining a representative aliquot presents a problem. Sometimes a solid precipitate introduces a complication in an otherwise homogeneous medium. And sometimes a large solid object is submitted that may have small areas of highly concentrated contaminants but, if pulverized and prepared as a unit, weight concentration would yield data that did not properly represent the nature of the problem.

There is need for thoughtful evaluation of samples and their physical characteristics. An important function of the personnel engaged in sample receipt, recording, and handling is the extra effort and careful attention to detail including documentation at this stage that can prove important when data use questions arise later.

Sample preparation procedures can range from simple extractions to complex methods for separation and emulsification. Novel procedures for sample preparation are being developed but are yet untested. Homogenization of samples containing volatile organic compounds (VOCs) is not recommended because of the high potential for VOC loss during sample manipulation. Carefully controlled headspace methods are often the best alternative for the analysis of VOCs.

The presence of radioactivity in a sample imposes unique requirements on the analytical laboratory. Whether or not radioactive contamination is present is key knowledge needed for the subsequent treatment of the sample and for the characterization and remediation of the site itself. Information on sample radioactivity is also needed to define safe handling procedures and to protect laboratory workers and the facilities from radioactive contamination and exposure. This is part of DOE's ALARA principle, to keep radiation exposure "as low as reasonably achievable." Though samples should be screened for the presence of radiation before being submitted to a laboratory, there is widespread experience that often this is not done. A simple, quick radiation screening procedure would be very useful to the analytical lab. Presently, four procedures must be done to ensure that samples do not contain radiation: gross alpha, gross beta, liquid scintillation, and gamma scan. (This characterization is in addition to the health physics monitoring by probe and smear for alpha and beta/gamma activity normally done on radioactive samples upon receipt at a radiochemical laboratory.) This rigorous pre-testing is expensive and time-consuming. If *a priori* site knowledge gives the analyst reason to suspect radiation, safeguards must be taken. If it is feasible to perform only one test, the recommended method is liquid scintillation.

When sample preparation must be customized for particular sample types, as with heterogeneous samples, it is critical that careful record keeping be done to document the condition of the sample-as-received and to detail all procedures performed upon the sample. The positions of sample receivers, handlers, and preparation personnel should be staffed with highly qualified personnel; if possible, these positions should be upgraded to reflect the importance of these jobs.

Project Planning

General Requirements

The effective and appropriate planning and management of a study to analyze heterogeneous hazardous wastes demands a cooperative effort between project management, field scientists, and the laboratory project manager. This cooperation should begin with a carefully focused experimental design that is based upon realistic and agreed-upon DQOs, as described in Chapter 3.

The need for close communication between client and laboratory personnel is especially pronounced when the job entails heterogeneous hazardous waste characterization. Unconventional sample handling and preparation techniques may be required; thus a laboratory representative should be a part of the project planning team. Close attention to formulating achievable DQOs will save later trouble by clearly defining the specific needs of the particular analytical regimen. It is essential that DQOs be tailored to the project objectives; establishing DQOs that are too rigid merely places an extra onus of responsibility on the laboratory personnel. Communication with the project manager should not end at the planning stage. Indeed, continued contact and consultation is key if the proper decisions are to be made while allowing the most flexibility to the analytical laboratory.

It is important that the analysis request be complete. The request should contain:

- A clear, complete description of the sample preparation, extraction, and analysis procedures that will be required, including detailed performance specifications.
- Documented reporting requirements.
- A listing of the required reference and performance evaluation materials.
- Mechanisms for the laboratory to obtain technical assistance from the EPA in implementing or gaining approval of method modifications or performing non-routine methods.

When routine methods do not exist for a particular characterization, it is usually because lower detection limits are required, an unusual combination of chemicals is present, the sample matrix is complex, or the sample/analyte type is unique to a particular site.

Analytical laboratories that wish to undertake the complex preparation and analysis of heterogeneous hazardous wastes may need to procure special equipment ranging from fusion crucibles to large volume centrifuges. Special mechanical reduction mills will often be needed, and they must be located in a different part of the laboratory from the routine sample preparation area (because of added dust and vibration). For non-routine analyses, the laboratory should have highly trained personnel and instrumentation that is not dedicated to production work, especially if new methods or untested modifications are requested.

Quality Assurance and Quality Control

For the purpose of heterogeneous waste characterization, project specific QC protocols should be developed. Project planning should address the homogenization of samples in the field, if possible. If this is precluded by field conditions or sample complexity, the laboratory may attempt to homogenize the sample to obtain a representative aliquot. Once the material has been homogenized, existing laboratory QA/QC protocols are readily amenable to sample characterization.

There are certain minimum criteria that must be met by analytical laboratories charged with the responsibility of generating environmental data to support waste management and environmental investigations. Such criteria have been well documented for the analysis of waste. National consensus standards for environmental data operations have been developed by multiple organizations. For example, the DOE has adopted the ANSI/ASME NQA-1 standard. EPA's Quality Assurance Management Staff (QAMS) has developed QA/QC program standards for its regional offices and its research and development laboratories. The Nuclear Regulatory Commission has issued QA guidance for low-level waste disposal sites, and the Department of Defense has developed different approaches for implementing QA/QC among the different services. In addition, the ASTM committee D-34 on Waste Disposal is developing a QA/QC standard. The intent of each program is to assure the technical integrity of the data collection process and to assure all data are of known quality. Presently the American Society for Quality Control is working with representatives of the various agencies that have developed QA/QC standards to meld key elements and concepts of NQA-1 and EPA QAMS guidance so that conflicts between the various requirements can be resolved.

The total error associated with waste characterization is the sum of population and measurement errors. The measurement error associated with any data set is a composite of collection, handling, transportation, subsampling, and analytical variabilities (see Chapter 4, especially Table 4-2). Due to the complexity of defining and collecting a representative sample from a heterogeneous population, the sources of error associated with the sample collection process are likely to be the major factor. In comparison, error associated with analytical measurements would generally be expected to be much smaller.

Sample Receipt, Handling, and Preparation

General Considerations

As previously discussed, to meet sampling and analytical program objectives, there must be iterative communication between sampler, analyst, and data user. Standard operating procedures (SOPs) for collecting, handling, and subsampling of samples will be determined by the project's data quality objectives.

Unless information indicates otherwise, the analyst assumes that field sampling was done properly and that the sample received at the laboratory is representative of the material of interest. The assumption that the total sample is representative of the waste of interest is not necessarily transferable to subsequent aliquots used for analysis unless consideration is given to subsampling error potential. Though it is generally accepted that the greatest source of measurement error is the field sampling step, the responsible laboratory manager must take care to mitigate small but additive errors in the subsampling and analytical steps.

When a sample is received at the laboratory, a stepwise characterization procedure begins. Figure 6-1 is a flow chart of the analytical plan. Clearly, the nature of heterogeneous hazardous waste dictates that strict safety procedures coupled with good laboratory practice must be observed throughout the process.

The first step upon sample receipt is the proper inspection and safety screening of the sample. The laboratory chain of custody begins here, and there must be careful documentation of all operations performed on the sample. Any gross abnormalities or contradictions of the field sample documentation should be brought to the attention of the laboratory manager (1).

Because sample matrices and types of contamination are widely variable, many treatment and analytical judgments must be made. It is advisable that experienced analysts, in consultation with sampling personnel, decide which subsampling strategies should be used.

Several steps may be involved in the progressive analysis of heterogeneous samples. It is important to consider *a priori* knowledge in deciding upon specific analytical procedures because each step taken can potentially change the composition of the remaining sample.

In all cases, a documentation of appearance is necessary. When the presence of radiation is suspected, it is necessary to screen for radioactivity. For multiphase samples, it is important to observe and record an estimation of the phase ratio. If a visual inspection determines that a sample contains more than one phase, the project manager should be consulted to discuss the merits of homogenization versus individual phase analysis. Each phase of a multiphase sample may be of particular interest.

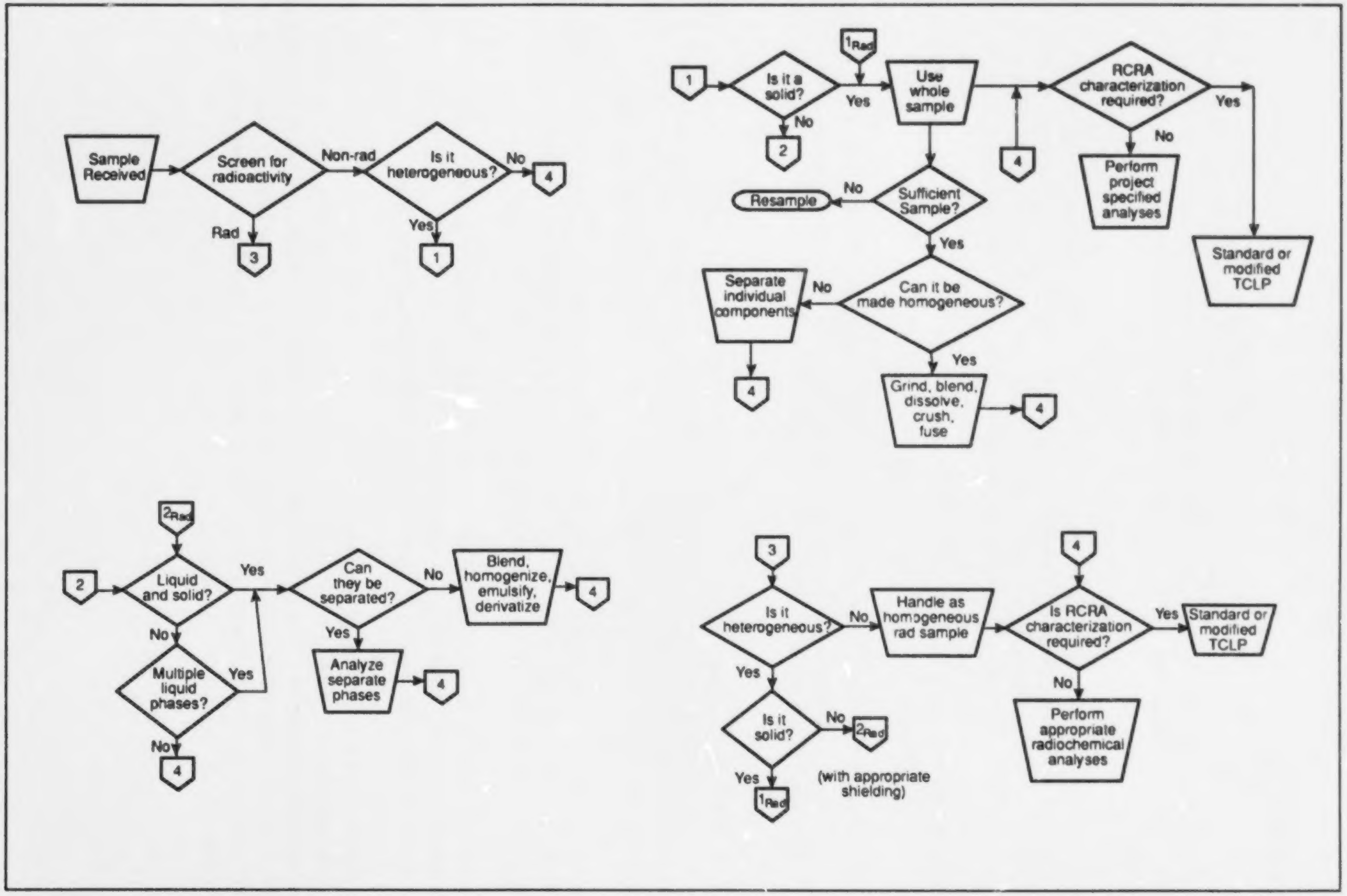

Sample Received
Screen for radioactivity
Rad
3
Non-rad
Is it heterogeneous?
No
4
Yes
1
1
Is it a solid?
No
2
Yes
1Rad
Use whole sample
4
RCRA characterization required?
Yes
Standard or modified TCLP
No
Perform project specified analyses
Sufficient Sample?
No
Resample
Yes
Can it be made homogeneous?
No
Separate individual components
4
Yes
Grind, blend, dissolve, crush, fuse
4
2Rad
2
Liquid and solid?
Yes
Can they be separated?
No
Blend, homogenize, emulsify, derivatize
4
Yes
Analyze separate phases
4
No
Multiple liquid phases?
Yes
No
4
3
Is it heterogeneous?
No
Handle as homogeneous rad sample
4
Is RCRA characterization required?
Yes
Standard or modified TCLP
No
Perform appropriate radiochemical analyses
Yes
Is it solid?
No
2Rad
Yes
1Rad
(with appropriate shielding)

Figure 6-1. Decision tree for sample preparation and analysis.

Sample Preparation

Samples composed of several phases (each of which is homogeneous) can be separated and analyzed separately for metals and organic constituents. Another possibility is to mix the phases to achieve a homogeneous sample and remove aliquots for metals and organics analysis. Heterogeneous solids can be ground up to achieve a homogeneous sample for metals and semivolatile organic analyses. The entire sample of heterogeneous material can be analyzed for volatile constituents, or the sample may be extracted with methanol or polyethylene glycol (PEG) and an aliquot analyzed. If there is superficial contamination of large particles, leaching tests can be performed.

Separation

One basic option available to the laboratory in dealing with heterogeneous waste is to separate out discrete sample elements. This approach works primarily for liquids or mixtures of liquids and solids. Consider a sample that contains three discrete layers: an organic layer on top, a water layer in the middle, and a solid at the bottom. Often the sample will have separated during shipment, and the analyst can take an aliquot of each layer for analysis. The analytical results are then combined mathematically using the weight and the concentration found in each layer.

Sometimes an individual layer can be further separated. Samples from oil refineries often contain a "rag" layer which consists of an emulsion of oil, water, and solids. This rag layer has a density greater than oil but less than water. This layer is homogeneous when sampled; however, upon addition of solvent (e.g., hexane and/or acetone), the solid material drops out of the emulsion. In this case, the layer can be separately analyzed for the material dissolved in the solvent and the solids.

Homogenization

The second basic option available to the laboratory is homogenization of heterogeneous samples. In this case the sample is cut, ground, shredded, etc., to achieve a homogeneous material that may be sampled. This technique is restricted primarily to solid samples that will be analyzed for metals and non-volatile organic compounds. There are several types of laboratory grinders on the market that can be used to homogenize soils and debris.

Liquids can be homogenized to some extent; however, sample integrity will be compromised if the phases begin to separate during aliquot removal. An ultrasonic bath or horn can be used to aid in dispersing separate layers long enough to get a representative aliquot of the sample. Another option is to add an emulsifying agent or surfactant to the sample followed by ultrasonic mixing. Non-ionic surfactants, such as polyethoxynonylphenol can be used to disperse oil into water. Use of emulsifying agents, however, introduces the possibility of adding contaminants which are of interest in the sample, thus raising detection limits. They may also cause interferences in subsequent analysis, particularly if they coextract with organic contaminants of interest. Use of ionic surfactants may avoid some of these problems. For routine analytical work, emulsifying agents or surfactants are not generally recommended because of these problems. Furthermore, it is not possible to know *a priori* whether a particular emulsifier/surfactant will work on a given sample.

Whole-Sample Analysis

One way to avoid the issue of heterogeneity is to analyze the entire sample provided. If the entire sample is used, the issue of heterogeneity is not germane as far as the laboratory is concerned. Heterogeneity may still represent a problem from a field sample standpoint since the lab can only provide results as good as the sample itself permits.

This approach is really only feasible for volatile constituents due to sample size constraints; however, it represents a real possibility for heterogeneous solids. Solid samples may be taken in a 40-mL vial with septum seal. At the laboratory the vial is weighed. The vial may then be submitted to either a heated headspace purge or water (5 mL or more) may be introduced and the vial coupled directly to a purge unit. The purged gas is collected on the normal volatile trap for subsequent analysis by gas chromatography or combined gas chromatography-mass spectrometry. Several manufacturers make heated head space purge units capable of analyzing the entire sample in a 40-mL VOA vial. After analysis the vial is emptied and weighed to determine the exact sample size.

Another approach which represents analysis of the entire sample for volatile organic constituents is to extract the sample using methanol or PEG. The entire sample (in a jar or in a 40-mL VOA vial) can be extracted with methanol and a portion of the methanol introduced into the purge chamber of a purge-and-trap device. The assumption is that all volatile components from the sample are extracted into the methanol (or PEG) and an aliquot is analyzed. Normally the amount of methanol introduced depends on whether the project requires quantifying the more volatile constituents (i.e., the gases). Typically 5 to 25 µL of methanol is used. If higher volumes are used, the early part of the chromatogram is obscured and the detection limits for the more volatile constituents are increased.

Sample Digestion, Extraction, or Fusion

Once the sample aliquot is selected, the sample is further prepared for analysis. For metals this normally involves digestion with strong mineral acids. Extraction with methylene chloride, hexane, or acetone is used for semivolatile organics, and purge-and-trap or direct injection may be used for volatile organics.

Heterogeneous aliquots can be digested for metals analysis. One technique for achieving the digestion is to use a microwave-assisted digestion method or a bomb technique. The microwave digestion works well for aqueous and organic liquids and solids; however, the sample size is limited depending on the amount of organic material in the sample. For pure organic materials (i.e., oils) only about 0.25 gm is recommended due to pressure buildup in the Teflon digestion vessel. Newer digestion vessels are capable of higher presures and slightly more sample can be used; however, one should select sample size carefully. Organic solvents should never be digested due to rapid increase in pressure during heating. Sample bombs (Teflon lined) may also be used; however, they are likewise limited in sample volume.

Organic liquids and solvents may be analyzed directly for most metals by dilution with an appropriate solvent (e.g., kerosene, toluene, methyl isobutyl ketone) and direct introduction into the ICP or Flame AA. If using this approach, an internal standard is highly recommended to account for changes in sample viscosity. The internal standard is preferable to the more tedious method of standard additions.

Samples that require organic analysis will be extracted using one or more organic solvents. The resulting extract is homogeneous and can be diluted or concentrated to the desired concentration range. Volatile organics are analyzed using the purge-and-trap technique. Purge-and-trap can be used on large sample sizes and thus can be used to advantage with heterogeneous samples since the analytes end up in a homogeneous (gas) phase.

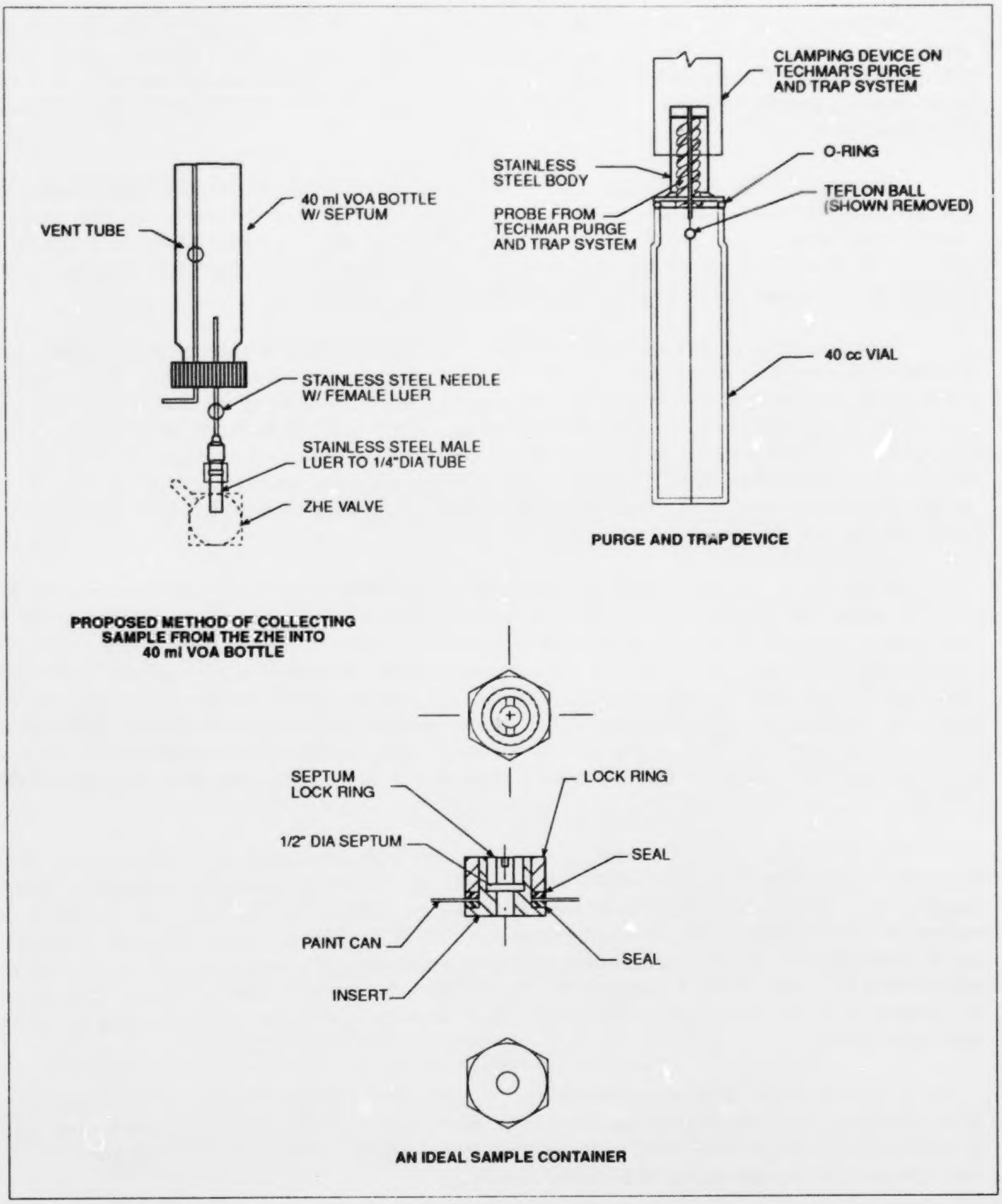
Samples contaminated with volatile organic compounds must be subsampled, handled, and treated by special procedures due to the potential for volatile loss during handling. Participation of laboratory personnel in the planning of field sampling for VOCs (and all other contaminants) can help in the selection of proper sample collection containers and will facilitate subsampling in the laboratory. The three drawings of Figure 6-2 illustrate various innovative sampling and shipment vessels. Two of these are ready for purge-and-trap analysis without analyst intervention. The other is an engineer's drawing of an "ideal" shipping container, complete with septum port and an insert sleeve for various indicators (2).

A sample preparation technique that is primarily used for the analysis of metals in solid matrices is high temperature fusion (see Chapter 5 for field applications). Sample preparation by high temperature fusion was originally developed for X-ray fluorescence (XRF) and arc/spark emission spectroscopy. X-ray fluorescence is particularly susceptible to the effects of sample heterogeneity (particle size, orientation and surface roughness). By use of fusion, a homogeneous glass disc is prepared, and analytical errors due to particle physical properties are eliminated. However, interelement effects, which may be severe in XRF, need to be compensated for in order to obtain accurate results. Recently, sample preparation using fusion has been applied to ICP analyses.

Fusion is accomplished by mixing a suitable flux with the sample in an appropriate ratio (between 1:1 and 10:1, flux:sample) followed by heating the mixture in a suitable crucible in a muffle furnace up to a maximum temperature of 1200 Deg. C. Once the flux becomes molten, it is maintained at temperature for 15 to 20 minutes so that the sample matrix is dissolved. The melt can be poured into a dilute acid solution, either hydrochloric, nitric, or aqua regia, or allowed to solidify in the crucible. If the latter procedure is followed, the solidified disc is removed and placed in a Teflon or plastic beaker, diluted acid solution is added, and the disc is leached until complete dissolution occurs.

Fusion methods have some limitations. In many cases fluxes which have the same purity as an ultra-pure acid are not available. Thus high blanks may adversely affect detection limits. Also if the flux and/or temperature used to prepare a sample is inappropriate, losses of the more volatile elements such as tin, antimony, and arsenic may occur.

Fusion methods have many advantages. In many cases it is difficult or impossible to dissolve matrices, even with the use of hydrofluoric or perchloric acid. Difficult matrices such as silicon carbide or refractory brick are examples. Fusion methods may also be quicker than standard digest-


VENT TUBE
40 ml VOA BOTTLE W/ SEPTUM
STAINLESS STEEL NEEDLE W/ FEMALE LUER
STAINLESS STEEL MALE LUER TO 1/4"DIA TUBE
ZHE VALVE
CLAMPING DEVICE ON TECHMAR'S PURGE AND TRAP SYSTEM
STAINLESS STEEL BODY
O-RING
PROBE FROM TECHMAR PURGE AND TRAP SYSTEM
TEFLON BALL (SHOWN REMOVED)
40 cc VIAL
SEPTUM LOCK RING
LOCK RING
1/2" DIA SEPTUM
SEAL
PAINT CAN
SEAL
INSERT

PURGE AND TRAP DEVICE

PROPOSED METHOD OF COLLECTING SAMPLE FROM THE ZHE INTO 40 ml VOA BOTTLE

AN IDEAL SAMPLE CONTAINER

Figure 6-2. Samplers that allow the entire sample to be analyzed for volatile constituents.

ions using acids. Finally, fusions allow for the use of much larger sample sizes in the sample preparation stage. Both microwave and oxygen bomb techniques are limited to samples weighing a few hundred milligrams. Fusions do not have this restriction. Thus there is a greater chance of employing a more representative sample in a fusion technique.

The Effect of Particle Size

Generally, the larger the sample the better when dealing with heterogeneous materials. Large samples, however, may not always be feasible when performing micro analyses. One approach to circumventing this difficulty is to follow the guidelines set forth in Pierre Gy's sampling theory (3; see also the discussion in Appendix B). To minimize subsampling error, Gy's theory suggests a minimum sample size that increases as the size of the largest particle increases. These "minimum" sample sizes are larger than the normal samples used in environmental analysis. Sometimes the analytical subsample size can be increased or the size of the subsample that is digested or extracted can be increased. Then a subsample of the well-mixed digestate or extract can be analyzed. Another approach involves aliquoting a sample of the required size into several smaller subsamples that can be digested or extracted and then analyzed individually or as a recomposited sample.

Table 6-1 gives the maximum particle size allowable for normal sample size, according to Gy's theory. If the maximum particle size is greater than that listed in the table, particle size reduction (PSR) is suggested. Fortunately, if *a priori* knowledge exists about the sample or the mechanism of contamination, the use of large sample sizes or PSR may be avoidable.

Table 6-1. The Relationship of Sample Size to Maximum Particle Size

SUBSAMPLE SIZE (grams)	MAXIMUM PARTICLE SIZE[a] (centimeters)
1	.1
2	.13
3	.14
4	.16
5	.17
10	.21
20	.27
30	.31
40	.34
50	.37
75	.42
100	.46[b]

[a] The maximum particle size allowed can be approximated for other sample sizes by using this equation: Maximum particle size = the cube root of (sample size in grams x .001).

[b] The Toxicity Extraction Procedure and the Toxicity Characteristic Leaching Procedure allow samples to contain particles as large as 0.95 centimeters.

References: Maney (4); can also be calculated from (3).

Leaching Tests

For heterogeneous wastes, leaching test results may better represent potential hazards to humans and the environment than would mass-concentration data for particular analytes. With large items contamination is likely to be superficial and mass data of little relevance to hazard. Also, standard laboratory protocols for the digestion of environmental samples preparatory to analysis do not always work well for larger particles or synthetic materials. Of course, the choice between whole-sample analysis and a leaching test is made during project planning, not in the laboratory upon receipt of samples.

Often, the leaching test that is mandated is the Toxicity Characteristic Leaching Procedure (TCLP). The TCLP is required whenever RCRA applies; that is, if it is to be ascertained whether the waste is a characteristic hazardous waste, or if the success of waste treatment before land disposal is to be assessed. The nominal sample size for the TCLP is 100 grams.

With wastes containing large items, the project planners must decide whether to subsample and leach portions of the items that appear to be "hot spots," or to ascertain representative contaminant values by extracting random subsamples from a number of different items. If the latter course is chosen, a subsampling scheme must be devised. When the items are of varied composition, another order of complexity is introduced. In this case, the investigator may choose to leach subsamples of the different types of items separately, then composite the results mathematically on a weight or volume basis.

Innovative leaching tests are not performed with any frequency in hazardous waste characterization. However, in some cases they may be eminently appropriate. For "worst-case" leaching scenarios, standard batch leaching protocols can be altered to use harsher solvents, or aqueous eluants of high or low pH. For leaching large items, standard tests can be done with specially-constructed large leaching apparatuses. If particle size reduction to a standard, fine grain is not performed, longer leaching times may be appropriate. The disadvantage of a large-scale test is the volume of waste solvent generated. However, this may be offset by the need for far fewer leaching tests to attain representativeness. The application of innovative leaching tests (or any non-standard procedures) must be cleared by the regulatory agency during project planning.

Innovative Techniques

Radiation Screening Parameters

It is important that laboratories recognize the need for proper screening of samples that are suspected of containing radioactive materials, and it is critical to recognize the limitations and strengths of various screening devices. The laboratory's license for dealing with radioactive materials will dictate its need for and use of screening equipment. (It must be emphasized that, for sampling and sample shipment of radioactive materials to be in compliance with regulation, a thorough radiation screen must have been performed in the field.)

Radioactive material is the physical material which, by the process of nuclear decay, emits some form or forms of radiation. For the purpose of discussing the screening of samples, only the three principal types of radiation need be considered: alpha, beta, and gamma radiation. Because of the different absorption characteristics for each type of radiation, different detection systems are required. Both alpha and beta emitters may also release gamma radiation as part of their decay, but no single screening method is adequate to detect all forms of radiation being emitted from a sample.

The screening of samples that may contain radioactive materials serves many purposes. This screening:

- provides health and safety protection for laboratory personnel
- provides guidance on correct shielding, clothing, and monitoring to be used
- directs the sample through an authorized and appropriate subsequent analysis
- provides information for a radioactive materials inventory
- fulfills administrative and licensing requirements pertinent to compliance parameters

In deciding on appropriate radioactive screening protocols it is essential to understand the reasons for performing the planned screening. In some cases, a simple screening with a Geiger-Müller probe or a NaI probe is adequate. But, if more specific data are needed to protect personnel from inhalation and ingestion hazards, a series of scans for alpha, beta, and gamma rays may be necessary (5, 6).

Several detectors are available for gamma or X-ray emissions, alpha emissions, and beta emissions. Each has both advantages and limitations, as shown in Table 6-2.

Table 6-2. A Comparison of Several Radiation Screening Devices

Emission Type	Detector	Advantages	Limitations
I. Gamma, X-rays	Geiger-Muller	Sensitivity	X-rays may be absorbed
	NaI	Measures bulk of sample	No information about isotopes emitting alpha, beta rays
	Germanium	High resolution	Must be kept at liquid nitrogen temperature
	Pressurized ion chambers	Integrates sample activity	X-rays may be absorbed
	Thin window probe	Measures low energy photons	
II. Alpha	Alpha scintillation	Many probe geometries available	Only good for surface or near-surface sources
	Gas-flow proportional	Higher counting efficiency	Fragile window
III. Alpha, Beta	Sealed-gas pancake detector	Sensitive to both radiations	Alpha sensitivity much less than beta sensitivity
IV. Beta	Beta-gamma pancake probes	Sensitive to beta	Not good for alpha scan
	Beta scintillation	Rugged	Lower counting efficiency Smaller area covered Must be close to source Not sensitive to ^{3}H or ^{241}Pu
	Tritium detectors	Hand-held Sensitive to ^{3}H	Need large surface area

One of the most versatile detection systems for use in screening is the liquid scintillation counter (LSC). In this system a small amount of sample is placed in a counting vial, and a liquid scintillation cocktail is added. The total volume of the vial is usually 5 to 20 milliliters. Any alpha or beta radiation is absorbed by the cocktail and the energy is emitted as light. The light is counted by photomultiplier tubes. Advantages of this system are high counting efficiencies and sensitivity to forms of radiation least likely to be detected by gamma systems. Thus use of an LSC system and removal of small amounts of sample provides the broadest coverage of potential radioactive isotopes. Although LSC is not particularly sensitive to high energy gamma emissions, gamma rays are usually emitted in concert with a mode of decay (e.g., alpha or beta), which is easily detectable by LSC. By the use of LSC, it is possible to do an excellent broad screen for radioactivity, although the use of an unprocessed sample may preclude precise quantitative results due to quenching and other effects. This method is particularly applicable to liquids. It is also applicable to solids if small amounts of the sample are placed in the cocktail or if smears of the sample are placed in the cocktail (a smear is a small piece of filter paper, cloth, polystyrene peanut, or foam that has been used to collect small amounts of sample by rubbing a surface). A less expensive system than the LSC can be implemented by using a hand-held device such as a pancake style alpha/beta detector or a scintillation detector fixed to a simple planchet holder device. One disadvantage of this system is the relatively low counting efficiency for some isotopes, in particular, tritium.

A laboratory which has concern for all types of radioactive materials might be best served by setting up an LSC system. A laboratory which prefers not to set up an LSC system can utilize multiple monitoring systems to provide coverage for the various types of radiation potentially present in the samples. Such systems can be set up relatively inexpensively and provide adequate information for personnel protection. Ancillary elements of the screening system, in addition to procuring the correct hardware, will include appropriate calibration of the equipment, routine (at least daily) performance checks for equipment, and training of screening technicians in the operation, application, and limitations of all equipment used.

A disadvantage common to all screening systems for alpha and beta activity is the necessity of opening the sample containers. Although this requires breaching sample integrity, it is the only way to obtain valid screening data for pure alpha or beta emitters. In laboratories where this is not appropriate in the sample receiving area, it may be necessary to screen for dose rate in one area and alpha/beta in a second, sample processing area.

Special Requirements for Analysis of Mixed Waste Samples

Support for DOE's Environmental Restoration and Waste Management program presents a challenging opportunity to the analytical laboratory. Past operations of the DOE facilities have left a legacy of both homogeneous and heterogeneous mixed waste requiring physical and chemical characterization to determine appropriate disposition according to treatability and regulatory requirements.

The presence of radioactivity in waste samples collected for RCRA hazardous waste characterization mandates special handling in the analytical laboratory (7). Correct guidelines for safe handling of radioactive samples should be established by the laboratory. For example, health physics guidelines at the Oak Ridge National Laboratory (ORNL) limit the total activity of "very high" radioactivity isotopes (such as ^{90}Sr) to 0.1 microcuries for monitored benchtop sample preparation, 10 microcuries for radiochemical hood work, and 10 millicuries for glove box operations (8).

Researchers at DOE National Laboratories are experimenting with analytical techniques for the analysis of radioactive wastes and mixed wastes to meet the objectives of RCRA SW-846 testing (9). Because of the lack of standard regulatory methods for the RCRA analysis of radioactive wastes, researchers are exploring sample preparation techniques and modifications of existing EPA protocols (SW-846 methods and Contract Laboratory [CLP] methods) to address this immediate need.

At ORNL research and development efforts have focused on the analysis of volatile organic and semivolatile organic contaminants in radioactive waste samples. Tomkins et al. (5) have described the adaptation of SW-846 method 5030 for glove box use. In this manner, the volatile organic analysis may be completed in a remote non-radioactive laboratory using conventional EPA GC/MS techniques.

The analysis of semivolatile organics in mixed waste via current regulatory protocols may present an unacceptable safety hazard due to the level of activity present and the large volume of material to be extracted (typically a 1 L aqueous sample) (6). Reduction of sample size in the extraction step is an alternative but at the expense of analytical sensitivity. Continuous liquid-liquid extraction is preferable to the conventional separatory funnel technique since direct operator contact with the radioactive samples is minimized. In another useful technique, Tomkins and Caton (7) have demonstrated the use of commercially available solid-phase extraction cartridges to minimize the analyst's exposure to the radioactive sample and to effectively separate the radioactivity from the analytes of concern. These also generate minimum waste from the extraction step.

Neutron Activation Analysis

The technique of neutron activation analysis (NAA) is a powerful elemental method capable of measuring many elements in a variety of matrices. In general, it is very sensitive, with low detection limits for environmentally important elements such as arsenic, selenium, the halogens, and many metals which exceed the capabilities of other commonly available analytical techniques. The method lacks sensitivity for a few key elements of particular environmental concern. These include lead, copper, and cadmium. When properly utilized for the determination of those elements for which it is most suited, NAA can contribute to the overall characterization of hazardous materials.

Because the sensitivity is very good for many elements, the sample sizes generally used for NAA are very small; less than one gram and often only milligrams. In most applications, the ability to use a small amount of the material to be analyzed is a distinct advantage. In addition, the requirement for sample handling and preparation for analysis is greatly reduced compared with other techniques which require solubilization. Samples can be analyzed as solids, liquids, or even gases, and the elemental determinations are not dependent on the chemical state.

A major advantage NAA brings to characterization of heterogeneous materials is its application to macrosamples, that is, the direct analysis of very large samples, perhaps kilograms or even eventually a 55-gallon drum (10). Both the excitation source (neutrons) and the analytical probe (gamma-rays) are very penetrating. Given the proper facilities for irradiation and counting, there is no reason large samples cannot be assayed for many analytes. While analytical imprecisions will arise because of the uncertainty of the location of the analyte within the sample volume, the level of uncertainty likely will accommodate the data quality objectives for gross analysis or screening. The construction of such a facility at a large site would minimize the required handling and transport of hazardous materials. The cost of this specialized technique may be at least partially offset by the elimination of the need for sample homogenization, segregation, etc., required by any other technique.

At the Center for Chemical Characterization and Analysis at Texas A&M University, preliminary studies on the feasibility of developing a "large sample" NAA facility are underway. The program is still in its infancy, but some progress has been made. One initial finding was that the element cadmium, which is of great environmental concern, was not determinable using conventional NAA at the expected levels of interest. A variation of NAA called prompt gamma activation analysis (PGAA), however, is very sensitive for cadmium (11). A separate PGAA procedure for cadmium is under development. The PGAA method using isotopic neutron sources for activation is also likely to be field portable, possibly allowing field screening of wind rows or landfills directly without excavation or sample removal (see Chapter 5 for further discussion of field applications).

A variation of the NAA technique which has been highly developed for certain mining applications and for bore-hole logging is fast neutron activation analysis (FNAA). Although the sensitivity is not particularly good for certain elements of concern such as lead, FNAA may be appropriate for use as a screening tool (12).

Waste Disposal in the Analytical Laboratory

In the process of performing an analysis, laboratories generate waste. Laboratories are subject to the same RCRA regulations as are industrial production operations. However, wastes generated by the laboratory can differ significantly from wastes generated at industrial production operations. The American Chemical Society's Task Force on RCRA has prepared a handbook to aid generators of laboratory waste in determining the appropriate responsibilities for proper waste disposal (13).

Satellite waste collection containers at the analyst's work station may pose a safety hazard if not properly vented, because all laboratory salvage must remain in a sealed container except when waste is added or removed. Safety concerns such as pressure build-up from vapors or potential chemical reactions from the mixing of waste forms must be addressed in the laboratory waste management plan. Modifying the waste collection vessel by adding a vent tube with appropriate absorbent, such as charcoal for organics and carbonates for acids, is a possible solution (14).

When processing heterogeneous wastes, laboratories may end up with large volumes of excess sample and extract. Little guidance is available to laboratories regarding disposition of excess sample. Two general options are available for sample disposal: return unused and unmodified sample to the sampler (generator) for disposal or arrange disposal by the analytical laboratory. While disposal options are straightforward, the actual process can be complex if heterogeneous or radioactive samples are involved. Each option for disposal has advantages and limitations. These are noted in Table 6-3. 40 CFR 261.4(d)(1) allows exception to the RCRA regulations for handling and storage of samples for analysis and the return of excess sample to the generator. Sampling of heterogeneous waste requires close coordination with the laboratory to assure sufficient sample size is submitted for analysis yet assure minimal sample remains for disposition by the laboratory.

Most waste disposal procedures are specified in regulations. The mechanism of excess sample disposition should be specified in the project work plan. The project planners should be responsible for determining potential hazards and safety considerations for sample disposition. Such information should accompany the samples to the laboratory.

Reporting Requirements for Analysis of Heterogeneous Waste

Reporting the results from the analysis of heterogeneous hazardous waste entails an expansion of the usual reporting requirements. The report should include all pertinent information about the condition and appearance of the sample-as-received (15). Other report highlights that are particularly informative in the case of heterogeneous samples are: detailed descriptions of any sample screening analysis that preceded the requested analysis; an outline of the sample preparation steps and any observed phenomena that occurred; and a reconstitution of the sample if a series of analyses were performed on segregated subsamples from the same sample.

Table 6-3. Sample Disposal Options

Option A - Laboratory disposes of all sample excesses

Pros:	(1)	Most convenient for the project as a whole
	(2)	Site manager avoids storage and disposal problems
	(3)	Trained chemical personnel handle samples
	(4)	Eliminates unnecessary transport of materials
Cons:	(1)	Potential safety hazard to laboratory personnel
	(2)	Insufficient information may accompany sample to determine proper disposition
	(3)	Adds to overhead cost of laboratory operations

Option B - All sample excesses returned to waste site

Pros:	(1)	Eliminates potential hazards from sample mixing
	(2)	Avoids storage problems in laboratory
	(3)	Responsibility and cost of disposal handled as with remaining on-site waste
Cons:	(1)	Storage, handling problems for site manager
	(2)	Additional transport of samples
	(3)	Return of sample to site may not be possible
	(4)	May require reanalysis for waste acceptance criteria
	(5)	Potential for RCRA or CERCLA liability if altered sample is returned to site

Reporting requirements should be specified when requesting all chemical data and should include the following:

- Summary of analytical results for each sample
- Results from QC samples such as blanks, spikes, calibrations

- Reference to standard methods or detailed description of analytical procedures
- Raw data printouts for comparison with summaries

Most standard methods specify some set of reporting procedures. Analytical services programs such as EPA's Contract Laboratory Program present a set of specific reporting procedures as a contractual requirement (16,17). This has led to the designation "CLP" reporting package, a term that is correct in reference to CLP Routine Analytical Services methods.

It is critical that the laboratory keep clear and specific records of the physical characteristics of the sample on receipt, because a single heterogeneous sample may require segregation of components before analysis. The records should include size, weight, visible components, and any information that can be derived from visual inspection. If sample components are segregated before analysis, descriptions of each component, including weight/volume measurements or percent of total sample, should be provided in the report. It is frequently recommended that photographs or even video documentation be used.

The laboratory should describe the sample preparation procedures used in the analysis in enough detail that the data user can understand how the sample was manipulated during analysis because this may affect the usability of the data. For example, if the sample was ground, some inorganic analyses may be biased depending on whether the grinder had metal or ceramic components. If the sample was extracted with an organic solvent, components that do not leach from the sample under normal conditions may be detected (e.g., decomposition of rubber gloves in organic solvents may cause false positive response). In many of these cases, once the sample is prepared, it may be analyzed in the same manner as a homogeneous sample.

The project manager should consider requesting that the results of analysis of individual components be reported, in addition to a total sample content, in cases where the waste consists of discrete elements that were segregated before analysis. That will allow recalculation of site concentrations if one component is heavily contaminated or if individual components are contaminated with different analytes. It will also facilitate development of alternative strategies for remediation, including treatment of only the most contaminated fractions.

If an innovative procedure or a new application of a known procedure is used for sample preparation or analysis, a detailed description of the procedure should be provided. The description should include the measurement principle as well as examples of expected interferents, dynamic range, and other pertinent factors. Although laboratory and field chemists may be familiar with these methods, they may be unknown to the data user and errors in interpretation of data may occur.

Conclusions and Recommendations

Many research efforts can be described that will lead to improvements in the analytical procedures used for heterogeneous hazardous waste. Basically, they fall into three categories: sample preparation, instrumentation, and documentation. The preparation steps range from the design of a clear decision path to the development of special sample containers that will allow ease of handling while maintaining sample integrity. Instrumentation needs should include the evaluation of various methods for sample emulsification, fusion techniques, and continuing refinement of screening equipment. Documentation is important for the establishment of new procedures and their implementation in the laboratory. It is crucial, too, for the concise description of the sample-as-received.

The unusual nature of heterogeneous hazardous waste presents a challenge to researchers in all areas, from sample handling to data interpretation. Careful planning of this research will pay off in simplified and focused analysis in the decades ahead.

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Chapter 7

The Larger Perspective

Roy R. Jones, Sr.

Introduction

The preceding chapters demonstrate that the application of conventional sampling approaches to heterogeneous waste is very difficult and frequently provides unsatisfactory results. The problems presented by heterogeneous wastes and debris are complex and interdisciplinary. When the question of available technology to deal with such materials is considered, another order of magnitude of complexity is introduced.

Among the principal conclusions to be drawn:

- Because the methods for heterogeneous waste characterization are not as well developed as those for conventional environmental media, a common nomenclature has not been adopted by those working in this field. The confusion of terms (and, hence, expression of concepts) impedes communication among professionals and hinders progress in this area.

- The potential pitfalls in study planning, as encountered during the DQO process, are more acute for heterogeneous waste studies than for other environmental studies. This makes it imperative that reasonable, site-specific study goals be emphasized, which in turn may lead to devoting more project resources to study planning.

- In designing the heterogeneous waste characterization study, investigators have a very wide variety of statistical models to choose from. Insofar as possible, they should make use of historical and process data, and data obtained by non-intrusive methods. Study design may be seriously constrained by worker health and safety considerations. A design with several stages of data collection and evaluation, rather than one massive effort, may be very cost-effective.

- Existing QA/QC methods are seriously inadequate for heterogeneous waste studies. A new set of modified methods must be developed. In this effort, the development of site-specific comparison or reference materials to improve both QA and QC should take priority.

- An enormous suite of field methods is already used with heterogeneous waste. In addition, there is a vigorous research effort directed towards developing field instrumentation. A strong trend towards field measurement and analyses is evident.

- Laboratory personnel must know what to expect in samples from the heterogeneous waste site. An analyst must be part of the study planning team from its inception, and the laboratory may need special equipment to handle unusual samples. Laboratory logistical, safety, and waste disposal problems may be greatly exacerbated by heterogeneous samples, especially if they contain radioactivity.

Heterogeneous waste sites can be placed in three general categories:

- those sites with problems amenable to current methods of waste characterization
- sites where current strategies or technologies of waste characterization are unsatisfactory, but methods now under development (or methods used in other industries) offer great promise
- sites for which current approaches, even augmented by new methods, probably cannot yield "representative" waste characterization

For these latter sites, we must change the way we go about the characterization studies and probably change the questions we ask. The discussion that follows summarizes these three types of situations and recommends general measures to expedite the characterization of heterogeneous hazardous wastes.

Successful Waste Characterization

Most large waste sites, to one degree or another, may be considered heterogeneous. As long as the question of "Hazardous Wastes" is not a concern, the materials may be handled with relative ease and dispatch by conventional segregation, reduction, and disposal techniques. Materials representing an economic benefit may be salvaged and recycled, modified by reduction (shredding, grinding, compacting, etc.) and/or composting, and the residues disposed of by incineration, burial, etc. Dangerous materials may be dealt with by the safest expedient means, particularly by re- or over-pack and shipment to a hazardous waste facility.

Where hazardous chemicals or radionuclides are of concern, there are several factors that may enhance the likelihood of successful characterization. Obviously, conventional methods work best when the wastes are not very heterogeneous. There are standard methods for sampling liquid-filled drums. A single kind of production waste, with perhaps a second phase that can be separated from it, is amenable to characterization (see Appendix A). Piled or containerized wastes the investigator can be confident are only superficially contaminated may be handled by wipe tests followed by some type of washing.

We also succeed when we ask less difficult questions. Studies aimed at simply identifying the contaminants present, or confirming/denying the presence of one particular contaminant, have a better chance of attaining their DQOs than those requiring rigorous quantitative, "representative" sampling. These types of questions are asked when, for example, contaminated industrial equipment is to be sold for re-use in the same industry, or is to be treated as scrap and melted in a blast furnace.

Process knowledge concerning the creation of the heterogeneous wastes aids in successful waste characterization. When the contaminants of concern can be narrowed to a small number *a priori*, project resources can be allocated towards more samples and fewer per-sample analyses. For sites that originally operated as dumps or waste reprocessing facilities, it is of great benefit to establish early that some or most of the wastes present could not be contaminated; they can then be dealt with as ordinary debris. Process knowledge is of most use for DOE sites and those regulated under RCRA. It is often unavailable for CERCLA sites.

Finally, investigators can sometimes look for contamination solely in the environmental media surrounding the waste, and not attempt to characterize the waste itself. Conventional monitoring techniques can be used, and the need for waste handling is obviated. This strategy may be applied to some DOE and RCRA sites, and it is an option for CERCLA sites that are municipal landfills.

Methods Development

As described in the preceding chapters, there are many promising methods whose further development would aid in the characterization of heterogeneous hazardous wastes. These include field analytical methods, statistical project design tools, sample handling techniques, and QA/QC methods. In addition, there are undoubtedly study design and implementation tools currently being used in other technical disciplines that could be adapted to heterogeneous waste characterization.

Communication among professionals will be the key to enlarging the suite of methods brought to bear on heterogeneous waste sites. As one example, there is a need for a new and continuing effort within EPA and DOE and jointly staffed by both. What is needed is the formation, support, and use of an "Applied Technology" Group, Office, or Committee. Broadly speaking, this group of technical specialists would continue to work in the spirit and intent of the Heterogeneous Waste Characterization Workshop. It would serve as a focal point for:

- The continued preparation and dissemination of an accepted glossary of words and phrases needed to assure clear communications between agencies and disciplines. The definitions herein were included only for the purposes of this discussion; they can in no way be considered as "official" definitions of any agency, unless they were drawn from regulations published in the Federal Register.

- Inter- and intra-agency innovative technology projects, maintaining lists of availability and modifications of methods.

- Investigations of state-of-the-art extramural technologies, with an eye toward acquisition and incorporation of technologies from other industry disciplines into hazardous waste site operations.

- Development and maintenance of an Applied Technology "bulletin board" posting information accessible to all EPA regional offices and DOE facilities.

There is no need to create an entirely new organization. The organizational elements already exist within the different agencies and the private sector, and, in some cases, they are duplicating effort. For example, the Department of Energy has an Office of Technology Development. The Department of Defense maintains programs and facilities in each department. In the U.S. Army, there is the Corps of Engineers; the Navy has the Naval Facilities Engineering Command, Environmental Quality Division. The Air Force program is the Engineering Services Center Environics Division. Because of defined security responsibilities and classification systems within these agencies, some technologies and processes will always be justifiably restricted from public access. However, those that are not classified would share in the technology evolution with the rest of the hazardous waste handling community, and the classified sector could benefit from the developments of the proposed consortium.

EPA has both a Technology Transfer Program and a Technical Support Program. They are developing capabilities with contractors, consultants, and national trade associations such as ASTM. Based on this beginning, EPA, DOE, and DOD could initiate a federal consortium charged with creating improved communications and interchange of ideas in the non-classified areas of hazardous waste problem solving.

Other Federal agencies and departments have long and productive histories of developing and applying scientific/engineering technologies to the solution of problems. If the initial consortium can successfully deal with "turf" and "not-invented-here" syndromes that are the main impediments to interagency cooperation, other agencies and departments should be anxious to join in the efforts.

A Changing Perspective

The intractable problems posed by heterogeneous materials will not be solved simply by better communication among hazardous waste professionals. Nor should we anticipate rescue through the application of ever-more-sophisticated technologies to ever-smaller samples. There are instances where the waste characterization questions now being asked cannot be answered through any effort of reasonable magnitude. The drum of assorted laboratory wastes (Figure 1-1) is such an instance. The question *Is any item in the drum contaminated to a level above the action level?* can be answered when there are only a few items per drum and a few drums on the site. For practical reasons the question is unanswerable when there are many drums or many items per drum, and no technology now on the horizon will change this. For such situations, fundamentally new approaches to waste characterization are needed.

There are many sites that are not amenable to the classical approaches for the selection of samples to be considered "representative" of the site. If, early in the site investigation and/or subsequent site characterization phases, a site or critical portions of the site could be designated as "Heterogeneous Hazardous Wastes Areas," they possibly could be exempted or temporarily waived for an additional defined time period from some of the restrictive regulations that now confound site studies. This site/portion would be the last area to be approached as a unit and would serve to temporarily store identified, characterized hazardous wastes that were not amenable to the characterization and treatment techniques applied to the rest of the site. These would still be heterogeneous, but they would be characterized and quantified amounts of waste that could then be manipulated, treated, or over-packed for ultimate disposal as required to prevent their escape into the environment. The final regulatory goals would have to be satisfied eventually, but the heterogeneity of the materials would not impede the conventional handling of those other portions of the site wastes more easily dealt with. An economy of scale or at least a reduction in problems introduced by waste variability could be achieved.

By such controlled manipulation and on-site accumulation and temporary storage, not only would some segregation and volume reduction be accomplished, but the remaining heterogeneous hazardous material might then be more amenable to statistical treatment. If the manipulation could include some unit processing operations such as sorting, grinding, or homogenization, the final resultant products could be a quantity of homogeneous waste, either hazardous, dangerous, or acceptable, and another quantity of very highly contaminated hazardous waste. This approach is not possible under current restrictions placed on the handling of waste by "treatment" regulations or interpretations of technically weak or loose regulations. This makes applications of new or innovative technology to problem solving very difficult or impossible to implement.

Ultimately, the actual solution to these waste accumulations may lie in approaching them from a different viewpoint using methods imported from other industries. One possibly fruitful approach is that used in the mining industry. There is an analogy between a heterogeneous waste site and an ore body. Both may contain deposits of valuable material. While the economic benefits of an ore accrue to the producers of the material recovered, the value of treating a heterogeneous waste site is not strictly a function of the value of the components recovered. However, any recovered component of value reduces the cost of removing the environmental threat posed by the original site.

Furthermore, the "waste" residues from the "mining" of a waste site are an identified and characterized waste stream that may be sequentially treated to prevent or reduce future environmental problems with the waste. By establishing a specific series of unit operations as a processing scheme, the waste site may be dealt with in a manner that demonstrates actual progress almost from the start of operations rather than an indeterminate period of study and then re-study of the study. If initial activities can include tangible benefits for the surrounding community, either aesthetic or economic, public awareness expressed as negative concerns may be modified into positive community activities.

Sampling has evolved along defined paths that reflect the matrices perceived to provide the most likely route to affect an organism exposed to that matrix. The most obvious routes, inhalation, ingestion, and, to a lesser degree, adsorption and absorption, focus attention to air, water, and actual contaminants in sediment, soil, or product residues. In most of these cases, the question of whether a sample is "representative" of a given area or volume is amenable to statistical analyses. As long as wastes are present in relatively discrete and definable areas or volumes, ranges of particle sizes, and numbers of phases present, the conventional methods of taking a representative sample work.

If there is to be acceptable progress in dealing with the heterogeneous areas of hazardous waste accumulations or sites, sampling technology must evolve actively into the acquisition of data from site "hot spots." Just as new characterizations and identifications of waste produce new problems and lead to new technologies of manipulation and treatment, so must new approaches be developed dealing with the identification and characterization of the wastes. Characterization and treatment of heterogeneous waste accumulations must be recognized as an iterative design and implementation process. In some cases, radically different approaches may be required. Sampling may become an element in a series of unit processes that actually alters the physical structure and distribution of the components of the waste.

Initial clean-up and removal activities provide the best opportunity for identifying and characterizing the waste materials on the site. They can also include preliminary manipulation and segregation of the hazardous materials remaining for remedial activities. While this may be deemed "treatment" and cause some regulatory problems, it would provide the opportunity to expedite the final resolution of the site problems more rapidly and at less total expense to the taxpayer and the responsible party.

This chapter and the preceding chapters developed from an interdisciplinary scientific and technological viewpoint. It was not the purpose of the authors to enter the area of policy and planning for either EPA or DOE. However, numerous technical approaches that were advanced by workshop participants had to be qualified "but the regulations don't allow that." This problem of overly-rigid regulations for waste sites has been addressed in detail by the National Advisory Council for Environmental Policy and Technology (NACEPT) (1). In its report, NACEPT has documented the regulatory impediments to innovative site study and waste transport and treatment techniques. Additional institutional barriers exist where there are multiple agency jurisdictions and conflicting regulations. This has been recognized by EPA and DOE, and there has been a growing cooperation between the two agencies as expressed in the activities of the "Harmonization" committees and other interagency groups active for the last few years. It is a sincere hope that as problems evolve, so do solutions, and that this report will be a contribution to more effective solutions to some of the problems.

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APPENDIX A

Appendix A

Hypothetical Case History Drum Characterization

Tom Starks and Gretchen Rupp

Background

In 1983 the new owner-operator of XYZ Specialty Metals came under pressure from the state RCRA agency to clean up the wastes stored on the plant property. Of principal concern were two unlined lagoons, each containing more than 2000 cubic yards of chromium sludge. After a brief engineering study, it was decided to solidify the sludge chemically and store the product on site in drums. A small concrete batch plant was set up next to the lagoons. The sludge was excavated with a backhoe, mixed with water, fly ash, and Portland cement, and decanted into 55-gallon steel drums. The drums were labeled by lagoon, batch number, and within-batch drum number, and a drum inventory was recorded. Over a four-month period, all of the sludges were solidified. The resulting drums were stored on an asphalt pad on the plant site.

In 1990 the plant operator decided to build an addition on the plant. This required cleaning up those areas of the plant property where wastes were stored. Integral to the cleanup would be establishing that the drummed solidified sludges were not RCRA-hazardous and disposing of them at an off-site landfill. The consultant brought in to do the necessary studies established that these were not RCRA-listed wastes, but could not ascertain from process information whether they would qualify as characteristic wastes. The consultant made a walk-through examination of the drum storage area. At that time it was discovered that many drums were corroded, and liquid had apparently leaked from a number of these. Apparently solidification had been incomplete in some batches, and there was an alkaline supernatant several inches deep atop the concreted sludge in the drums filled from these batches. This had induced corrosion of the drums at the liquid-concrete interface. This situation was confirmed by a preliminary study that involved opening selected drums from a number of different batches. It appeared that about five percent of the drums contained free liquid.

The consultant investigated the original uses of the two lagoons and the details of the 1983 sludge stabilization. Lagoon A had been a flow-through settling basin. Lagoon B had been the disposal site for sludges dredged from Lagoon A. At the time of the sludge fixation, the sludge in Lagoon B had been fairly dry. The sludge was dry at one end of Lagoon A, but it graded to a saturated condition at the other end. In excavating the sludge, the operation began at one end of each lagoon and worked gradually to the other end. Excavated sludge was mixed with water, then blended with fly ash and cement. A single batch filled 10-15 drums. When the last of a batch was decanted, it was sometimes necessary to hose out the equipment to clean out the last of the mixture; thus the last drum might contain extra water. There were changes in process variables and equipment over the course of the operation. As the solidification operation was getting underway, the blend formula was altered several times. Different mixers and mixing tanks were used during the four-month period. There was a major equipment change between the processing of the A and B lagoon sludges.

Initial Project Planning

The consultant and the owner discussed the decisions that would have to be made before off-site drum disposition could proceed. The state regulatory agency would have to decide:

- whether a drum contained a hazardous waste. If so, that drum would have to go to a hazardous-waste disposal facility. If not, it could go to a municipal landfill (the consultant had first established that a local landfill would accept non-hazardous drums).
- how the corrosive supernatant in some drums would be treated as the drums were handled.

The owner would have to decide, on the basis of cost factors:

- whether it would be less expensive to dispose of the drums as a hazardous waste or to undertake an expensive characterization study in the hope of demonstrating their non-hazardous nature; and
- whether to go forward with site cleanup once the costs of the characterization study and drum disposition were known.

The owner did not set a maximum project budget, but indicated to the consultant that inordinate costs would compel him to postpone the project. No time constraints were identified for the drum characterization study.

At this point a RCRA specialist from the state regulatory agency was brought into the planning process. He and the consultant first discussed how to determine if the concrete was a hazardous waste. It was agreed that the characterization was to be done by vertically coring the full depth of concrete in selected drums, pulverizing the core, and performing a TCLP test on a subsample of the (well-mixed) powder. The TCLP extract would be analyzed for total chromium. If it exceeded the regulatory criterion (5 mg/l), the sample would be judged hazardous.

The handling of the liquid supernatant was discussed next. The consultant proposed a cursory study to establish average supernatant pH, RCRA corrosivity, and heavy metal concentrations. If these were within regulatory limits, any supernatant encountered as a drum was handled would be dumped out on the ground. The state RCRA specialist insisted that a considerable range in these properties could be anticipated, and therefore the supernatant must be separately characterized each time it was encountered. This would have entailed extraordinary analytical costs, so the following plan was agreed on. As each drum was handled, any supernatant would be siphoned out into a general holding tank. The collected, well-mixed supernatant would be characterized for those constituents regulated in the facility's NPDES permit. If it were within the specified discharge limits, it would be piped to the plant's surface water discharge; if not, it would be used up gradually within the plant as process feed water.

The consultant and his statistician now began planning the drum characterization study. They considered it important to take into account:

- differences between sludges from the two lagoons, especially since they were processed using different equipment;
- the changing nature of the wet mixture over time, as reflected in differences among batches; and
- the relative uniformity of the mixture within batches, except for the occasional "wet" drum at the end of a run.

In addition, the state RCRA specialist pointed out that drums on the outside of the stacks had likely had much more exposure to the elements, and the concreted sludge might be different from that in the interior of the blocks of drums. The 6120 drums of interest were stacked in eight separate blocks that were four drums across, three drums high, and 64 drums long. Since the interior drums in each block could not easily be surveyed, it was decided that the drums in the two exterior rows would be surveyed and disposed of first, and then the interior drums would be surveyed and disposed of. It was expected that the information obtained in the survey of the exterior drums would be useful in evaluating the population of interior drums, since the drums had similar origin.

Four of the blocks contained all 3050 drums, from 254 batches, filled with concreted sludge from Lagoon A, and the other four blocks contained the 3070 drums, from 256 batches, filled with concreted sludge from Lagoon B. There were 1514 drums in the two exterior rows of the four blocks from Lagoon A and 1534 drums in the two exterior rows of the four blocks from Lagoon B.

An exploratory survey of the exterior drums was performed to find the precision and accuracy of the proposed measurement process and to estimate the within-population and within-batch variance of log-transformed measurements of chromium concentration in the TCLP analysis of the concrete in the drums. The exterior drums were divided into four populations:

- Population 1 - all exterior drums from Lagoon A that were not the last drum of their batch
- Population 2 - all exterior drums from Lagoon B that were not the last drums of their batch
- Population 3 - all exterior drums from Lagoon A that were the last drums of their batch
- Population 4 - all exterior drums from Lagoon B that were the last drums of their batch

From the drum inventory, it was determined that Population 1 contained 1404 drums from 250 batches; Population 2 contained 1411 drums from 255 batches; Population 3 contained 110 drums; and Population 4 contained 123 drums. If selected drums contained liquid, the liquid was drained into the holding tank prior to sampling the concrete in the drum. The measurement process for the concreted sludge required that a 2 cm diameter hole be drilled vertically through the concrete in each selected drum from a randomly selected starting point on the upper surface of the concrete. The material obtained from the hole was mixed and then subsampled to obtain the 100 g laboratory sample upon which the TCLP analysis was performed. Each drum selected in the sample was weighed after removal of any liquid that might be present.

In the exploratory survey of the exterior drums, ten batches were randomly selected from each of populations 1 and 2 (with probability proportional to batch size, and with replacement) from among the batches that had at least two drums in the exterior rows. Two drums from each selected batch were randomly chosen. Of this pair, one drum was randomly selected and one sample was obtained from it by the method discussed above; three samples were obtained from the other drum. The three samples taken from one drum were obtained by drilling a hole in the concrete and then taking two subsamples ("splits") after mixing the material from the hole, and by then drilling a second hole (a "field duplicate" or "colocated" sample) and taking one subsample from the material obtained. With data from these samples, the consultant could estimate the between-batch variance, the within-batch variance, the within-drum variance, and the between-subsample variance (which also includes variances owing to handling and to analytical error). The sum of the within-drum and between-subsample variances represented the total measurement error variance for a single subsample taken from the material obtained from a single drill hole (employed here are some quality assessment procedures discussed in the chapter entitled, "QA/QC and Data Quality Assessment"). In the exploratory study, a sample also was taken from each of ten randomly selected (simple random sampling) drums in each of populations 3 and 4. These samples provided information about within-population variances for the end-of-batch drums.

The results of the exploratory study were that the measurements from all drums sampled were below the TCLP action level for chromium (i.e., 5 mg/l) with values ranging from 1.1 to 4.6 mg/l. The weights of the selected drums from populations 1 and 2 were very similar with a coefficient of variation of only 3 percent. The weights of the drums in populations 3 and 4 were quite variable (CV = 75 percent), and the mean weight of the drums in these populations was only 60 percent of that in the first two populations. The variance estimates for TCLP chromium concentrations obtained from Population 1 were sufficiently similar to those obtained from Population 2 data that the decision was made to pool the variance estimates. Of the total measurement-error variance for the log-transformed data, 90 percent was attributable to subsampling and analytical error. The total measurement-error variance was only 6 percent of the within-population variance and therefore was considered to be sufficiently small by the usual rules of thumb (i.e., error variance should be less than either one-tenth or one-sixteenth of population variance. The idea behind these rules of thumb is that further reduction in measurement error variance will not have sufficient impact on total within-population variance to make the attempted reduction worthwhile.). The estimated within-batch variance was found to be only 10 percent of the between-batch variance, which showed that relative to the variation between batch-mean concentrations, individual measurements were typically close to both the mean for the drum and the mean of the batch from which the sample was taken.

At this point the consultant and the state RCRA specialist explored the issue of how much confidence the state needed in its drum disposition decision and the sampling design that would be needed to assure this confidence. The specialist wanted to be 95 percent confident that all drums individually fell below the specified action level for the TCLP analysis. On this basis the consultant determined that one of two approaches might be followed. One approach would be to sample at least 95 percent of the drums. This would in essence imply that all drums be sampled, and those found, if any, that did not meet requirements would be sent to the hazardous waste facility. The second approach would be to randomly sample one drum from the "not last" drums in every batch and test whether the sample TCLP measurement was significantly below the 5 mg/l action level. If such a sample measurement from a batch was not significantly below the action level, they could then either sample all other "not last" drums in the batch to decide which needed to be sent to the hazardous waste facility, or send all "not last" drums in the batch to the facility without further sampling. All the drums that were the last drums of their batches would have to be sampled and tested as in the first approach. The second procedure, sampling two drums per batch, would require considerably less sampling, but the criterion that the sample measurements would have to meet to establish a significantly-below-action-level condition would be more stringent, and the procedure would be based on distribution assumptions that would be difficult to justify. The consultant calculated that the first approach would require approximately 6000 routine samples, while the second approach would require about 1000 routine samples.

The XYZ owner-operator could not justify proceeding with the plant expansion if it required 1000 or more TCLP tests of concrete cores. The consultant formulated an alternative, less-intense sampling strategy to support a completely different decision rule, and the state RCRA specialist agreed to this alternative. In this new plan, the state would only require that, for each drum population, the leachate from the aggregate of all drums of concreted waste must meet the TCLP action-level requirement. This would be demonstrated by showing that the leachate sample mean was significantly below the action level. This could be accomplished by taking a sample of drums that was much smaller than would be needed in the two scenarios discussed above.

The new sampling scheme is as follows. Within populations 1 and 2 (the "not last" drums), batches will serve as primary sampling units and be selected with probability proportional to batch size minus one (the excluded last drum) and with replacement. Batches that were selected in the exploratory study will be included in the population to be sampled, and, if selected, the data obtained from the first drum of the previous sampling will be used rather than taking new measurements. After batches are selected, one drum within each selected batch will be chosen by simple random sampling. In populations 3 and 4, sampling of drums will be accomplished by simple random sampling. Drums selected in the exploratory study will not be eligible for selection in this sample as results from the two studies will be combined to estimate mean concentrations for populations 3 and 4. The decision to include batches that had previously been sampled from populations 1 and 2, and to exclude drums previously sampled in populations 3 and 4, was to simplify the estimation procedures for population means and standard errors of means. The sampling with replacement of the batches recommended for populations 1 and 2 is somewhat unusual, but, in this case, while it will cause some loss in efficiency, it will greatly simplify the estimation of the standard error of the mean relative to the sampling without replacement procedure.

Acceptable false negative and false positive errors were established as follows. The regulator specified that the state would only be willing to allow the concreted sludge to be sent to the sanitary landfill if the mean TCLP were significantly less than the 5 mg/l chromium action level when using a one-sided 5 percent significance level test. Put another way, there would be a likelihood of 5 percent that any drum population having a mean TCLP chromium > 5 mg/l would be judged non-hazardous. The facility owner-operator, his consultant, and the consultant's statistician worked out the acceptable false positive error rate. They knew from the preliminary study that the mean concentrations for all the populations were probably about 3 mg/l. They also knew that, as 5 mg/l was approached, the sampling requirements for a given degree of certainty would increase greatly. Therefore, they specified a 95 percent probability that a drum population would be judged non-hazardous if its true mean TCLP chromium level were 3 mg/l. That is, in terms of tests of hypotheses, the signficance level of the test was specified as 5 percent, and the power (i.e., probability of accepting the alternative hypothesis, $\mu < 5$) of the test if the true value of μ is 3 was specified as 95 percent.

Study Design

Given these sampling goals and uncertainty constraints, the statistician proceeded to design the sampling scheme. He reasoned as follows:

For populations 1 and 2, a measurement of TCLP concentration of chromium would be obtained from a sample from one randomly selected drum from each batch selected in the batch selection process. If n is the number of batches to be selected in the sampling of a population h then the sample mean is

$$\bar{x}_h = \sum_{i=1}^{n} x_i /n, \qquad h=1,2$$

where x_1 is the measurement on the chosen drum from batch 1. The formula for the estimated variance of the estimator of the mean is (from reference 1, equation 6.21).

$$\hat{V}(\overline{x_h}) = (1/n)(\sum_{i=1}^{n} [x_i-\bar{x}_h]^2 \;/\; [n - 1]) = (1/n)s_h^2$$

The estimate of the standard error of the mean is just the positive square root of $\hat{V}\,(\overline{x_h})$.

The Central Limit Theorem comes into play here. Standardized sample means tend to the standard normal distribution as sample size increases. The confidence statements and tests of hypotheses employed here are based on the idea that the sample mean is normally distributed. To be significantly less than the action level, the sample mean must be less than the action level by 1.65 standard errors of the mean. The regulator's decision rule, therefore, is **If the mean TCLP chromium for population i is less than 5 minus 1.65 standard errors of the mean, the population will be judged non-hazardous, and all drums in that population can go to the sanitary landfill.** If it exceeds this value, that population is a hazardous waste. If one lets C represent the critical value that is the action level minus 1.65 standard errors, then the owner wants to have a 95 percent probability that the sample mean will be less than C when the true mean is 3 mg/l. To achieve this probability, the value 3 must be 1.65 standard errors of the mean below C, or in other words 3.30 standard errors of the mean below the action level. Hence for each population, one should have for standard error of the mean the value (5 - 3)/ 3.3 = 0.61 mg/l, or less. As observed in the preceding paragraph, the standard error of a population mean is a function of the within-population variance, s_h^2, and of the sample size for the population. Therefore, since the data from populations 1 and 2 in exploratory study provided a pooled estimate, $s_h^2 = 16.0$, the suggested sample sizes for sampling populations 1 and 2 are the same and that common sample size is the smallest integer n such that

$$[16.0 \;/\; n]^{0.5} \leq 0.61,$$

which is n = 43. It should be pointed out here that in determining sample means and standard errors, we are working with actual data, not log-transformed data. The log-transformations were necessary to stabilize variance so that a variance components analysis could be performed to determine the proportions of variance arising from various sources. But transformations are not used here because we may appeal to the Central Limit Theorem and because we are interested in investigating the means rather than variances.

For populations 3 and 4 (the "last-of-batch" drums), the sample mean must be a weighted mean since there are different amounts of concrete in each selected drum and we wish to estimate the average TCLP chromium concentration over the aggregate of all concrete in the population of last-of-batch drums from a lagoon. That is, if W_i is the true weight of the concreted sludge in last-of-batch drum i and T_i is the true mean TCLP chromium concentration for that drum, then we are interested in the value of $(\sum W_i T_i \ / \ \sum W_i)$ where the sum is over all last-of-batch drums in the population (3 or 4). Thus, the sample estimate of this value is

$$r = \sum_{i=1}^{N} w_i x_i \ / \ \sum_{i=1}^{N} w_i$$

where w_i is the weight of the i th selected drum minus a typical empty drum weight w_0 in the sample from a population. The estimate is in fact a ratio estimate where both numerator and denominator are determined from sample results. Therefore, a formula for the variance of a ratio of random variables must be employed before an estimate of the standard error of the weighted mean can be obtained. Let $\overline{w}$ be the arithmetic mean of the weights of all the drums (after removal of supernatant) minus w_0 in the sample from population. The estimated variance of the weighted mean is (from reference 2, Equation 4-21.4)

$$s_r^2 = (1 - f)(1/n)[\sum_{i=1}^{n} w_i^2(x_i - r)^2] \ / \ [(n - 1)\overline{w}^2] = (1-f)(1/n)s^2$$

where f is the sampling fraction n/N. The estimates of s^2 obtained for populations 3 and 4 in the exploratory study were so similar that they were pooled to obtain the value 25.0. Unfortunately, the Central Limit Theorem does not apply to ratio estimates and so we must appeal to the Chebychev Inequality which states that the probability that an estimate will differ from its expected value by more than k standard deviations is no more than k^{-2}. Because of the conservative nature of the inequality and the fact that it is two-sided while we are interested only in one-sided deviates, the regulator may be satisfied that the observed mean TCLP leachate concentration is significantly less than the action level if the observed value of r is four standard deviations less than the action level (i.e., confidence greater than 94 percent), and the factory owner will be satisfied if the value 3 mg/l is four standard errors less than the action level. Hence, the owner may want to choose a sample size n such that the standard deviation will be no greater than (5 - 3)/4 = 0.5. In this case, for the sample from population 3 which contains n = 110 drums, the owner will want n to be the smallest integer for which

$$(1 - n/100)(1/n)(25.0) \leq (0.5)^2.$$

The sample size required for Population 3 is n = 54. For Population 4, the population size is n = 123, and a sample of size n = 56 is needed.

It should be noted that the standard errors of the means or ratios that will be used in the significance tests will be estimates that employ the data from the final sampling study, not those from the exploratory study. Hence, the actual estimates employed may be smaller or larger than the target values (0.61 and 0.5).

The use of field duplicates and splits would continue in this study as in the exploratory study, but they would be used at a reduced frequency relative to the routine samples. However, at least 20 field duplicates and 20 split samples should be obtained. The number 20 is chosen because it provides estimates of variances that we can say are within a factor of 2 of the true value with 95 percent confidence. These QA samples should be uniformly spread through the routine sample stream. In addition, in populations 1 and 2, the statistician recommended taking a sample from one additional drum in ten of the chosen batches in each population to provide more information about within-batch variability.

The approximate minimum number of samples that would be obtained and TCLP tests that would be performed in this design would be 236. The consultant now compiled cost information to allow the owner-operator to decide on a course of action. The owner needed to consider whether the cost of the sampling and chemical analyses would be less than the savings in sending the four populations of drums to the sanitary landfill as opposed to sending the drums to the hazardous waste facility. If it were not substantially less than those savings, then it would be reasonable for the owner to declare the drums to be hazardous and not perform the sampling studies. If the cost of sampling and chemical analysis were considerably less than the savings and if the result of the investigation were that the sample mean, or weighted mean, were less (say, 3.6 mg/l) than the action level, but not significantly less than the action level, the consultant would recommend that the owner and regulator consider taking additional samples from the population to see if the additional data would provide the confidence required that the population mean were below the action level.

Once the exterior drums have been studied and disposed, the owner must then address the four corresponding populations of interior drums. If the sample mean or weighted sample mean for an exterior drum population is above the action level and there is no reason to expect that the corresponding population of interior drums will be different from the exterior drums, then it would be reasonable for the owner to declare that interior drum population hazardous and save the cost of sampling it. If the sample mean or weighted mean of an exterior population were found to be significantly less than the action level, then the owner should first try to show that the corresponding interior population has similar or better TCLP characteristics than the exterior population. For populations 1 and 2, this might be done by randomly picking 20 batches that were sampled in the exterior population and that also have drums in the interior population, randomly picking an interior drum from these batches and then performing a paired samples one-sided nonparametric test. This procedure cannot be applied to the two populations of last drums in batches. Also, since there were some batches that had no exterior drums in populations 1 and 2, the regulator considers it prudent to require that a sample be taken from one randomly chosen drum from each of these batches to ascertain that these batches do not yield TCLP chromium concentrations above the range observed in samples of batches that had exterior drums present.

If the nonparametric tests indicate the need for additional investigation of a population of interior drums from either lagoon A or B that do not contain the last drums in batches, the investigation of the population would follow a similar procedure to that employed for the corresponding population of exterior drums, but the additional information obtained in the sampling of exterior drums should be taken into account in estimating standard deviations and sample sizes. The two populations of interior last drums of batches from lagoons A and B will be sampled in a similar manner to the procedure employed for populations 3 and 4 of exterior last drums. The consultant will use information obtained in the sampling of populations 3 and 4 to determine appropriate sample sizes.

References

1. Raj, Des. 1968. Sampling Theory. McGraw-Hill, New York, 302 pp.

2. Hansen, M.H., W.H. Hurwitz, and W.G. Madow. 1953. Sample Survey Methods and Theory, Vol. 1. John Wiley, New York, 638 pp.

APPENDIX B

Appendix B

A Survey of Available Statistical Techniques

Leon Borgman

Introduction

The Waste Characterization Strategies work group included both professional statisticians and individuals with substantial experience in using and interpreting statistics in environmental applications. The group compiled the following list of statistical categories and subdisciplines that have been used or appear to have potential usefulness for heterogeneous waste characterization. The tabulation is quite impromptu and represents those topics which arose during a "brainstorming" session. Generally the more important and useful methods are toward the beginning of the list since they occurred to the participants first. References to literature and software are given for the most-used techniques. This list is far from complete as a guidance to project planners, but it could serve as a basis for the development of such guidance.

To place the methods within the context of heterogeneous waste characterization, many (but not all) have been classified within a multiple category framework. This consists of the following subdivisions:

Completeness of the statistical theory
A. The method is well established
B. Some questions remain
C. Many questions remain

Applicability to heterogeneous waste problems
I. The method would be applicable to heterogeneous drums
II. Homogeneous drums
III. Unconfined waste

Usefulness
a. Potentially a very useful method
b. Moderately useful
c. Not particularly useful

Data requirements
i. Considerable amounts of data needed
ii. Moderate amounts of data needed
iii. Useful with sparse amounts of data

The methods are classified into these categories on a preliminary basis; it may well be that with more investigation, the listed choices would be changed. Nonetheless, this listing should have some value as an initial examination of possible statistical techniques in heterogeneous waste characterization.

List of Methods

(1) Equiprobable pure random sampling

The population being sampled is regarded as a finite array of possible samples. No assumptions as to the probability law, statistical stationarity of the elements of the population, etc., are made. What is "out there" is just a collection of possible samples. The randomness is introduced by requiring that every possible sample have an equal likelihood of being included in the data to be collected. This is achieved by using a random number table or computer program to select which of the samples are going to be collected into the data set. One characterization of the technique is to say that "The population is deterministic; the sample is random" (1). The method is very objective and is particularly desirable if sample collection and analysis is relatively cheap so that very large data sets are feasible. The method is directed toward the estimation of the mean, variance, and similar parameters of the finite population of possible samples.

A; I,II,III; b; i

References: (2, Chapter 2; 3; 4, Chapter 4; 5; 6)

(2) Weighted pure random sampling

This is similar to (1) above, except that the possible samples are not collected in such a way as to make each equally likely to be included in the data. Instead, some rule is devised so that each sample has its own probability of being included in the data set. The weights can be based on the area of the strata from which the sample was selected, the size of the group from which the sample was taken, or the probability that an object of that size is encountered in the sampling procedure. This modification of random sampling is sometimes called "probability sampling."

A; I,II,III; a; i

References: (3, Chapter 2; 7, page 26)

(3) Stratified random sampling as a modification to items (1) and (2) above

The population of possible samples are divided into subpopulations, usually so that each subpopulation has less internal variation. Then the methods of (1) or (2) above are applied separately to each subpopulation. Some of the objectivity of method (1) is lost because the classification into subpopulations usually requires subjective judgments. A more even coverage of the population of possible samples (perhaps for contouring purposes) can be obtained with stratification than with method (1).

A; I,II,III; a; i

References: (2, Chapter 5; 4, Chapter 5; 5; 6)

(4) Systematic random sampling and/or cluster sampling

A rectangular grid, or some similar regular geometry, of locations to be sampled is laid out over the population of possible samples. The equal likelihood for inclusion of each possible sample into the data set is maintained by using some random mechanism to establish the placement and orientation of the grid in its exact position upon the population. For example, random numbers can be used to establish where the center of the grid will be placed, and then another random number can be picked to make a random rotation of the grid. The methods of (1) can then be used on the data. Some of the advantages of the method are that a very even coverage of the region for contouring or search can be achieved, and the logistics of sampling can be simplified (since the grid can be surveyed and staked previously and the samples can be collected in a rapid sweep over the grid).

A; I,II,III; a; i

References: (2, Chapter 8; 4, Chapter 8; 5; 6)

(5) Gy's methods for sampling homogeneous mixtures of granular materials

These techniques were developed in the context of the mining industry to sample crushed ore. The ore is thought of as consisting of an inert substance (gangue) and a valuable material (some metal or metals), which are intimately intermixed. Even though the ore is crushed to some degree of fineness, some of the value is hidden from the assay by a covering or armor of the gangue. The smaller the diameter of the particles, the more the value is released to be measured in the assay. The basic question, then, is "what sample volume and reduction of particle size is required to provide an estimate of the total value of the ore with a pre-specified accuracy or confidence interval?" The procedures depend on the characteristics of the ore and a substantial amount of calibration against practical experience. The best derivation of the basic mathematics of the method are given by Gy (8) in a paper in French. A recent exposition in English of Gy's derivation has been presented in a report by Borgman (9). The method appears to have applicability to waste characterization problems, although some trial and error will probably be required. The above discussion illustrates how Gy's sampling procedure extends from sampling statistics into sample collection and preparation. Thus, it seeks to provide an overall framework for sampling, whereas the traditional random sampling schemes address only the statistical aspects of data computation and leave questions of mesh size, volume of sample, etc., to the chemist. From this perspective, Gy's methods consider and involve many other practical sources of estimation error not included in the simple example used above to introduce the method.

B; III; ii
tailing piles: a
extreme intercorrelated heterogeneity: c

References: (8, 9, 10, 11, 12)

(6) Correlated spatial, temporal, intervariable geostatistical procedures (variogram, kriging, conditional simulation)

This is the general body of statistical techniques that have come to be called "geostatistics," although the methods are finding applications in many areas besides geology and mining. A more descriptive name is random field theory or random function theory.

In contrast to the various types of random sampling above, the assumption in geostatistics is that the population may be treated as though it is a realization of a random process; i.e., there is a probability law and various statistical assumptions concerning "stationarity" and "spatial intercorrelation" which model our uncertainty concerning the population. In contrast to the random sample model where "the sample is random and the population is deterministic;" in the geostatistics frame of reference, "the population is random and the sample is deterministic." This is interpreted to mean that the locations to be sampled can be selected deterministically (i.e., by subjective choice rather than by random numbers).

In most of the methods, the first step is to select the appropriate assumptions to mathematically model the population and to estimate from data or past experience a function that describes the spatial intercorrelation within the population (the variogram, the covariance function, etc.). Fortunately, many of the techniques are very robust relative to errors in these preliminary estimates; i.e., about the same answer is obtained even if the covariance function picked is somewhat wrong. Because of this, the covariance function (or variogram) is often picked subjectively in situations where there is very little initial information. As data are obtained, these estimates can be updated so that the final answers can be based on much better covariance estimates.

Kriging gives an unbiased estimate with minimum expected-square-error for the average of some attribute of the population over a specified spatial region of the population. There is a variety of different types of Kriging methods depending on the assumed statistical structure of the population and the one or more attributes to be estimated.

Conditional simulation is a body of techniques that produce by computer a detailed version of what the population might be, consistent with the measured data and the assumed statistical structure and spatial intercorrelations of the population. A number of such simulations can be produced, each of which agrees with the data and has the proper population statistical structure. These can be useful to characterize the degree of variability remaining after a suite of samples (data) have been collected from the population, either to help in finding future locations for sampling or to study the variation in possible responses to remediation action consistent with the amount of information embodied in the current data. If there is too much variation, more data can be collected.

Because of the subjectivity involved, the geostatistical procedures are much more in the spirit of engineering design. Much judgment is used, and experience, skill, and art are important factors. However, if properly used, the methods make a maximum use of the available data and are optimally cost-effective. Thus, they are appropriate for situations where sample collection and analysis are very costly and it is desirable to get as much information as possible from each datum.

The random sampling model and the geostatistical model are very different frames of reference. Both are valid and appropriate in various situations. There are also various elaborations of the random sampling model which take into account many of the structural features incorporated into the geostatistical model. The situation is analogous to the apparent conflict in physics between particle theory and wave theory. A fairly elaborate examination of the various considerations favoring one model over the other in a particular application is given by Borgman and Quimby (13).

A,B;
particularly suitable for III; a
may be useful for I,II; b

The amount of data needed depends on the balance permitted between objectivity and subjectivity allowed in obtaining the correlation/variogram functions.

if great objectivity is required: i
if substantial subjectivity is permitted: iii

References: (1, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22)

(7) Double sampling

The procedure proceeds in two phases or stages. A first data set is collected and analyzed. The information from this first set is then used to plan and perform the collection and analysis of a second set of samples. Within the random sampling models, the first data set is often used to obtain estimates of the population variance, and this provides guidance for picking the best sample sizes for the subsequent set of measurements. In the geostatistical frame of reference, the first data set is often picked to estimate or verify the variogram function selected and other structural assumptions made about the population, while the second data set provides the basis for a least cost computation of the estimates with the target precision.

Another common application of the method uses a large first screening sample with inexpensive analysis procedures, followed by a small second sample, carefully selected on the basis of the first sample results and analyzed with more precise, costly methods.

Procedurally and logistically, the double sampling process has much to recommend it in many situations. It is a very practical and reasonable tool for characterization of waste materials. A natural extension is to use more than two stages in the process (see items 8 and 9 below).

A; I,II,III; a; ii

References: (2, Chapter 13; 4, Chapter 6)

(8) Formal (Wald) sequential testing

These procedures are developed in the context of quality control. A sample of data is collected and used in a formal test procedure with three possible actions: (1) accept the null hypothesis, (2) reject the null hypothesis, or (3) take another sample of data. A formal stopping rule, derived under some choice of optimality conditions, is used to determine which of the three actions is most appropriate.

The advantage of the sequential methods is that the action level is reached with the smallest possible number of data measurements for a given power of the test. This is contrasted with fixed sample size procedures where the sample size is selected initially, and then the data are collected and processed. Usually, in order to guarantee the desired test power, a larger size of sample than needed is chosen as a conservative measure.

In contrast to the sequential, phased data collection discussed in the next section, the formal procedures here are very restricted as to the decisions which are made. Essentially one may accept, reject, or continue sampling relative to a formal test of hypothesis concerning some population parameter (e.g., mean or variance), usually with a likelihood ratio test. In the next section, the decision framework is much more loose and practical, allowing the introduction of intangibles, alternative courses of action, value judgments, etc. The formal Wald scheme may be a part of that, but it probably will only be used as a contributing source of information for the actual practical decision process. Thus, the method here is good for waste characterization if it is subsidiary to other methods. However, care must be exercised to make sure the underlying assumptions of the methodology are satisfied in the waste storage circumstances.

A; I,II,III; b; ii

References: (23, 24)

(9) Sequential, phased data collection and analysis (a more informal, "ad hoc" type of sequential testing)

This is an approach that is potentially very important for waste characterization, remediation, and monitoring. It is a natural extension of double sampling, can incorporate aspects of the sequential testing and procedures, can be used with either random sampling or geostatistical techniques, and generally allows the user to "proceed up the learning curve" in a way so as to make the required decisions with as little data as necessary. The sequential method is intentionally a loose, informal procedure which proceeds in alternating stages of data collection and judgmental interpretation. The project team must carefully define action alternatives, types of data needed at each stage, and so forth, but the sequential accumulation of information is not restricted to the formal Wald process discussed above. A sequential approach often allows the project team to avoid the over-expenditure usually associated with a single-stage process consisting of (1) plan sample, (2) collect sample, and (3) make decision. In order to guarantee that enough information is available for a safe decision, the number of samples collected is typically set conservatively large in the single-stage scheme. If the individual samples are expensive to collect and analyze, the cost of this conservatism can be substantial. The phased sampling approach avoids this by undersampling initially, then adding additional samples as needed to minimize the number of samples ultimately collected. There may, of course, be additional costs in placing contracts for each stage. These must be factored into the overall cost.

A; I,II,III; a; ii

References: (24, Chapter 8; 4, Chapters 6 and 7)

(10) Compositing (mixing) of diverse samples

Compositing is not a complete statistical technique in itself, but it can be used with many different techniques. Compositing is particularly useful where collection of samples is cheap and easy but analysis is costly, where relatively few (less than 20 percent) of the results are expected to be above the blank values, and where the goal is to estimate a population average. The samples are separated into groups, and the samples in a given group are mixed together (composited) to obtain a single group sample for analysis. The number of samples per group and the number of groups are determined by the requirements of the estimate accuracy and analysis accuracy. A type of composite kriging is presented and studied by Weight (25).

References: (4, Chapter 7; 25; 26; 27; 28; 29)

(11) Bayesian methods

At one time there was a very fierce debate among statisticians as to whether classical or Bayesian statistics are most desirable for use. Classical statistics were based on the use of prior information to design the mathematical model and assumptions for the statistical population but required that only newly collected data with proper randomization be used in making the inferences. Bayesian methods (based on a famous relation called Bayes theorem) required the subjective estimation of *a priori* probability laws be made by the user, then data collected and processed with the *a priori* probabilities to get *a posteriori* probability law. This was then used for making the statistical inferences. The subjective *a priori* probabilities are strongly involved in the results of the inference and, thus, two investigators can reach different conclusions from the same data if their initial opinions differed. Some statisticians found this very repugnant, since they wanted objective procedures that would lead all investigators to the same results. The Bayesian enthusiasts argued that in the real world, prior information is important and should be used to get as good an inference as possible with available data. It did not bother them that investigators could get different answers since this was not any different from other fields of engineering and science where judgment is an important component of any study.

Many of the same considerations arise in waste characterization. For compliance with regulation and for questions of litigation, highly objective procedures are advantageous. This suggests classical statistics and random sampling methods. However, where cost effectiveness is important (samples and analysis very costly), it is useful to introduce more subjective judgment to enable the utilization of smaller data sets. The Bayesian methods are one scheme for doing this in a systematic, formal way. The formal procedures may bury the investigator in mathematical difficulties, but an informal Bayesian approach (engineering and scientific judgment at each step of a sequential, phased approach) can be very useful. The previously mentioned methods of geostatistics, double sampling, phased and multistep sampling, and sequential testing and estimation are all methods which also attempt to allow the user to input prior information to arrive at greater efficiency and cost effectiveness.

A,B; I,II,III; a,b; i,ii

Reference: (30)

(12) Importance sampling

This is a new proposed procedure which tries to sample sequentially so that each new observation is collected at a location that is most important or significant to the decision or action being considered. The method needs more work for validation in practice, but it appears very promising.

C

Reference: (31)

(13) Bootstrap resampling/simulation for bias and confidence intervals with minimal data

There is considerable interest in obtaining confidence intervals for estimates and procedures which are so complex statistically that it is almost impossible to derive the intervals from mathematical manipulations. In this case, one answer would be to perform multiple sets of experiments and get a confidence interval from the value computed from each set. The cost of the multiple sets of experiments usually make this approach infeasible from budgetary concerns. A body of techniques that have come to be called "bootstrap methods" provides a sort of "poor man's confidence interval" that can be derived from a single set of measurements.

In this procedure, a single sample of *n* observations is used to provide an empirical distribution function for the population; then synthetic samples are developed by Monte Carlo procedures which imitate what one would have obtained with additional sets of *n* observations. The statistic or quantity of interest is then computed for each of many such additional data sets, and the histogram of the statistic or quantity is processed to provide a "rough" estimate of the confidence interval for the quantity. There is no intent to argue that this confidence interval will be as good as a confidence interval based on the full measurement sets; rather, it provides a rational procedure that can be introduced when time and cost prevent more elaborate measurement programs.

Various extensions of these procedures have been developed at the U.S. Army Corps of Engineer Waterways Experiment Station, Vicksburg, Mississippi, in the context of coastal engineering, and the results of these studies are just now beginning to appear in the journals (32,33,34). More applications are in press.

B; I,II,III; a; ii,iii

References: (35, 36, 37, 38, 39)

(14) Artificial intelligence, expert opinions, subjective probabilities (utility theory)

Sometimes useful where there is little or no data available, yet some planning or other action is necessary.

References: (40, 41, 42, 43)

(15) "Hot spot" analysis and search theory

The search for targets with a given shape (elliptical, square, etc.) with an appropriate grid which may be redefined as the effort proceeds.

A,B; I,II,III; a; i

References: (4, Chapter 10; 44, p289ff; 45)

(16) Extremal Analysis

Developed in engineering fields as a way to extrapolate to maxima or extremes. Should be useful for "hot spot" problem.

A,B; I,II,III; a; i

References: (46, 47, 48, 49)

(17) Censored or truncated data analysis

These methods are useful where the analysis method is incapable of detecting values beyond a particular threshold magnitude, or when data sets contain many "less-than" values. Only values above or below some limit can be measured. The data have been censored at some cutoff. How can one proceed with such data so they are properly included in calculations with other methods? Some research has been done on these problems, and the listed references will prove an entry into the literature.

References: (50, 51, 52, 53)

(18) Nonparametric (distribution-free) methods

This group of techniques uses rank order methods to obtain statistical procedures that are valid regardless of what the probability law for the parent population is. They are especially useful in waste characterization problems when little is known about the parent population and data are sparse.

There is a variety of nonparametric techniques covered by a very extensive body of literature. The methods often involve simple computational requirements and sacrifice very little "power" or decision accuracy as compared to parametric methods. The latter have more rigid assumptions that must be satisfied.

References: (54, 55, 56)

(19) Attribute (yes/no) testing, rather than numerical testing

The real question in many studies is "which action should be taken?" Various numerical measurements and their confidence intervals are only intermediary to the actual remedial action that is to be selected. However, there are methods in decision theory and other statistical fields that relate directly to the discrete selection process. This includes the area of cost-benefit analysis (57), which has considerable importance in most decision processes.

References: (57, 58, 59, 60, 61)

Although reference 58 is illustrated with applications from the petroleum industry, the methodology is useful in many contexts, including management of environmental waste.

The rest of the list is a tabulation of various other bodies of statistical techniques that may be relevant to waste characterization studies. There is no claim for completeness in this list, and almost certainly other topics could be included following further deliberation and discussion. The methods are listed here with appropriate references, but with only brief discussion.

(20) Proportion testing

Where the problems are concerned with the fraction or proportion of a population with a specified attribute, one can often use techniques, usually constructed around the binomial probability law, which produce estimates and/or make tests of hypothesis concerning proportions.

References: (2, 4)

(21) Control chart methodology and quality control

Methods developed in industrial quality control may find applicability in waste management practices. Reference 62 is a very old, but classical and very readable, introduction to traditional techniques. In the last several decades, however, there has been an explosion of new, and often somewhat controversial, procedures in this field associated with the names "Deming" (63) and "Taguchi" (64). Each of these "schools" of methods has its advocates and detractors. The new procedures are distinguished from the older type of quality control by their involvement with the whole process of production which leads to quality, and particularly the human element. There is less emphasis on just meeting contract specifications and more emphasis on striving to increase quality (or even achieve zero defects) by whatever ideas or methods can be found.

References: (62, 63, 64, 65, 66, 67)

(22) Compliance testing

This is really a subtopic within quality control which is concerned with testing to guarantee that quality specifications are met. It usually functions in a monitoring mode.

References: same as previous topic, plus (68)

(23) General multivariate methods (cluster, discriminate, classification, principal component, and factor analysis)

Most environmental data are actually multivariate in nature. That is, more than one quantity is required to characterize the situation and associated risks. Consequently, it is often artificial to pick one (perhaps dominant) property and make tests of hypothesis solely on that scalar quantity. There is a rich body of techniques that deal directly with the total vector of properties. These methods will probably find much greater use in the environmental context in the future.

References: (69, 70, 71, 72, 73)

(24) Source search strategy, as in locating source of a plume of contaminants in ground water

This can be viewed as a parallel to the "hot spot" search strategy of topic (15). Actually, both are subcategories of the field of pattern recognition and characterization. Much work has been done in recent years on pattern recognition relative to the analysis of remote sensing data from satellite measurements. References 74 and 75 give discussions of the topic from this more general perspective.

References: (4, Chapter 10; 44, p.289ff; 45, 74, 75)

(25) Decision theory techniques

In a general sense, this can be thought of as including all of the other topics in this discussion, as they influence decision-making relative to environmental concerns. However, the terminology is usually not used in that broad sense. Instead, it is generally taken to refer to a body of statistical procedures often related to economics and business management. These methods include decision trees and various simulation schemes.

References: (58, 76)

(26) System reliability theory for components and total system

Complex systems can sometimes be subdivided into separate components which behave independently, or act according to joint probability laws with other components. The study of how the reliability of the total system is related to the separate reliability of each component (or subgroup of components) constitutes system reliability theory. It may be thought of as a subfield of operations research.

Reference: (77)

(27) Risk analysis (related to decision theory)

Just as with decision theory, the area of risk analysis summarizes many aspects of the various topics in this list. It is usually restricted to decision-theory concerns. These often relate to economics, business management, and psychology.

References: (78, 79, 80, 81, 61, 82)

(28) Response surface techniques

This is a recently developed group of techniques which organize, usually with multiple regression methods, the search for maxima, minima, or other critical values of a variable or vector defined over a multidimensional space. Thus, it might have applicability to topic (24) in searching for the source of a plume of contaminants in ground water, or moving toward a maximum "hot spot" concentration in topic (15). However, the methods are much more general than those applications and seek to produce a multiple regression model of the variations of the variable(s) in the space of definition.

References: (83, 84, 85)

No attempt has been made to place the later topics (numbers 20-28) within the classification scheme used previously, since most are specialized techniques or broad general classes of methods that do not allow a general statement of appropriateness to waste characterization. For completeness, however, they are included.

It is clear that a large number of statistical methods are available. As a first step, the listing provides a set of possible approaches for characterizing a new situation for which the appropriate method is not obvious. It also underscores and emphasizes that the statistical methods for waste characterization are not "cut and dried" procedures laid out in handbooks, particularly when there is a large premium placed on cost-effectiveness. In large waste characterization and remediation projects, substantial savings may be possible with suitable initial statistical investigation of the most appropriate methods.

Clearly there is a need for some type of handbook, giving examples, evaluations, and comparisons of these various methods as applied to waste characterization. Such a book should carefully avoid being "captured" by any particular school of thought within statistics, but should include all possible ways to approach the problems in waste characterization.

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★U.S. GOVERNMENT PRINTING OFFICE: 1992-648-003/41817